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## XIII.—ATOMIC DIMENSIONS.

By R. G. LUNNON, *M.A., M.Sc.**Received September 29, 1925.**(Communicated by PROF. A. O. RANKINE.)*

## ABSTRACT.

The Paper deals with the diameters of the atoms of the elements, and compares the estimates obtained by various methods—viz., (1) Atomic volumes ; (2) X-ray analysis ; (3) Viscosity of gases ; (4) Van der Waals' equation and its modifications ; (5) Compressibility ; (6) Viscosity of liquids ; (7) Viscosity of solutions ; (8) Diffusion of ions ; (9) Mobility of ions in solutions ; (10) Latent heat of solution ; (11) Speculations as to atomic laws of force ; (12) Scattering of X-rays ; (13) Bohr's theory in the case of the hydrogen atom ; (14) Ionisation potentials ; (15) Band spectra ; (16) Chemical constant ; (17) Optical rotation ; (18) Molecular films ; (19) Langevin's theory of diamagnetism ; (20) Impacts of a stream of electrons on gas molecules ; (21) Density changes in permutite ; (22) Melting points of solids.

The results obtained by these methods, of which an extensive bibliography is given, are fairly accordant, and their mean shows that the addition of an inner electron shell gives an increase in diameter of roughly  $0.5\text{\AA}$ .

ESTIMATES of atomic and molecular dimensions have now been made in upwards of thirty different ways, and it is the purpose of the present Paper to collect and compare their results. The atomic volumes and X-ray crystal data will be considered first ; next the many other methods, each of which is applicable to a few elements only ; and finally the results of these methods are compared, taking the elements in groups. The results are shown graphically in each case, and a complete discussion of their relative merits is omitted, for brevity. Complete references are given at the end of the Paper, and a fuller comparison of some of the methods may be found in a summary by Herzfeld.<sup>(0)</sup>

The most extensive contribution to this subject has been the application of X-ray crystal analysis, and a partial summary of its results has been given by W. H. and W. L. Bragg.<sup>(1)</sup> In two different curves, the values of the "atomic radii" or "radii of combination," have been given for a large number of elements, and the parallel between these and the atomic volumes has been suggested. It is of value to re-state first the data of the Lothar Meyer curve of atomic volumes. The volume available for each atom of an element is easily calculated when the density of the element is known, and the cube root of this quantity is a measure of the diameter to be ascribed to the atom, if the atoms were packed as cubes, or as spheres in a simple cubic lattice. These figures have been re-calculated, and are presented in a new form (similar to that of the curves given by Davey<sup>(2)</sup>) in Fig. 1. The arrangement of the elements in steadily increasing atomic number is broken so as to give the same abscissa to all elements of the same group ; this means that the cube root of the atomic volume is plotted against the valency, with a special extension for the long periods. The value of this method is that it shows very clearly the regularity of the variation in atomic dimensions—a regularity which has greatly improved as more reliable data have become available. Of the 90 known elements, 18 have

not been measured, and all the rest except two (nitrogen and arsenic) follow the rule of increasing in "size" within their groups and are recorded in the figure. The curves cross each other only on the rare earth branch, when these two are omitted.

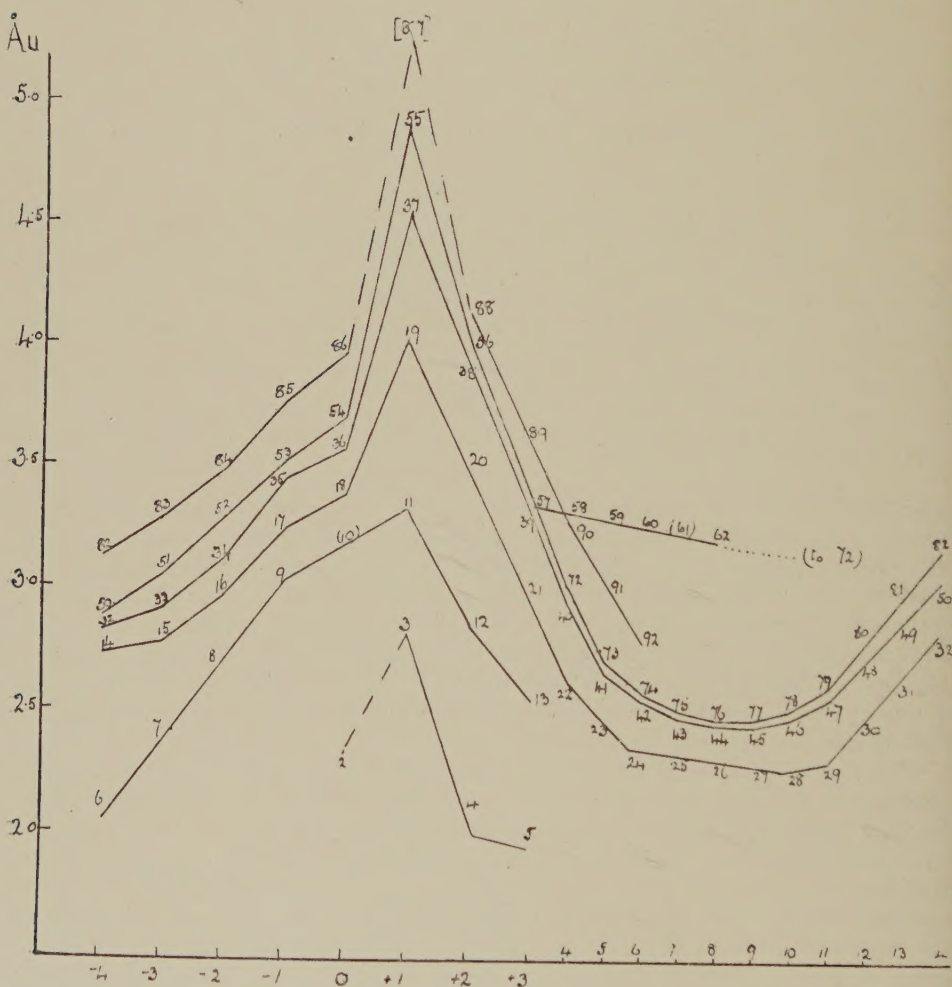


FIG. 1.—CUBE ROOTS OF ATOMIC VOLUMES.

In some parts of the curves the curves are exactly parallel. Biltz<sup>(3)</sup> has pointed out that the two following relations hold for consecutive elements:—

1. Atomic vol. of halogen =  $0.8015 \times$  at. vol. of rare gas.
2. Atomic vol. of alkali =  $1.823 \times$  at. vol. of rare gas -  $6.10$ .

The figures are certainly not final, chiefly because they are derived from densities



measured at various temperatures. Pierucci,<sup>(4)</sup> in pointing out that the density at the absolute zero should alone be used in these calculations, estimated that reliable data could only be given for 29 elements. Some careful estimates of "zero density" values have since been made by Herz,<sup>(5)</sup> using Lorenz's formulæ, and these we have included in our data, which therefore differ from the best earlier table, that prepared by Stefan Meyer<sup>(6)</sup> in 1915.

It is easy to pass from the volume of the space occupied by each atom to the volume of the atom itself, if the shape of the atom is assumed and the type of atomic packing is obtained by the methods of crystal analysis. Assuming a spherical atom, a fraction<sup>(7)</sup> 0.52 of the total space is taken up by the spheres if the lattice structure is a simple cubic one, 0.68 for a body-centred cubic lattice, and 0.74 for a tetrahedral or a face-centred cubic. It follows that the data of Fig. 1 can be used to give the atomic diameters, for the figures need, e.g., to be multiplied by  $\sqrt[3]{0.68/0.52}$  or by  $\sqrt[3]{0.74/0.52}$ —i.e., by 1.09 or 1.12—according to the crystal lattice. The curve of atomic diameters must therefore be similar to that of Fig. 1, for although the different types of lattice do not occur with a regular variation through the groups of elements, yet the difference between the factors for different lattices is very small. The actual results of X-ray crystal analysis are given by the curves of Fig. 2, and their shape confirms the above indication.

The assumption of sphericity in the atoms is unnecessary in the X-ray analysis, and the figures refer to the distance of nearest approach of two atomic centres, and this corresponds to a diameter. Only 40 of these are as yet available for elements in the crystalline state; they have been collected by Bragg,<sup>(1)</sup> Wyckoff,<sup>(8)</sup> Davey<sup>(9)</sup> and Scott.<sup>(10)</sup>

There are hardly any data of this kind for electronegative elements, and estimates of their size have to be made from polar compounds.<sup>(11)</sup> In these it is now clear that the atom does not behave as though it were a sphere of constant size; the space which it occupies, as an ion, depends upon the other elements with which it is combined. The atomic radius is not exactly an additive property in compounds. This is particularly clear in the complete set of figures for the alkali halides given by Havighurst,<sup>(12)</sup> for which an accuracy of one-tenth per cent. is claimed. It is sometimes useful, however, to retain the idea of the spherical ion, and Bragg retains the term "radius of combination." What is actually measured is the distance between the centres of two neighbouring ions of different kinds, and further deductions involve further hypotheses. Examples of two different views at this point are given by Bragg and by Davey, and Fig. 2 contains both sets of results.

For the most part, these curves run in rough similarity with those of Fig. 1. There is a striking difference, however, in the rising arms, for crystal data assign to the ions of the sulphur group elements and to the halogens a very much lower diameter than would follow from the atomic volume figures. This is probably due to the atom sharing electrons with its partner in the compound, and so approaching it more closely.<sup>(11)</sup> For the electro-positive elements, too, the ions in compounds are smaller than when free. The atoms of Ca in the pure metal are 3.93 Å. in diameter, and the ions of Ca in lime are 3.42 Å.

Similarly, in organic compounds the ionic sizes are not constant. Aminoff<sup>(13)</sup> records the measurement of the hydrogen diameter in two hydroxides as 1.15 in one and 1.05 Å. in another.

It has been stated by Davey<sup>(2)</sup> that the descending arms in Fig. 2 are exactly

parallel. There are, however, many exceptions to this rule, and the anticipations based upon it cannot be given much weight.

A more explicit relation of similar type has been given by Scott,<sup>(10)</sup> and relates to the inter-atomic distance in the crystal lattice. This distance,  $d$ , is held to be

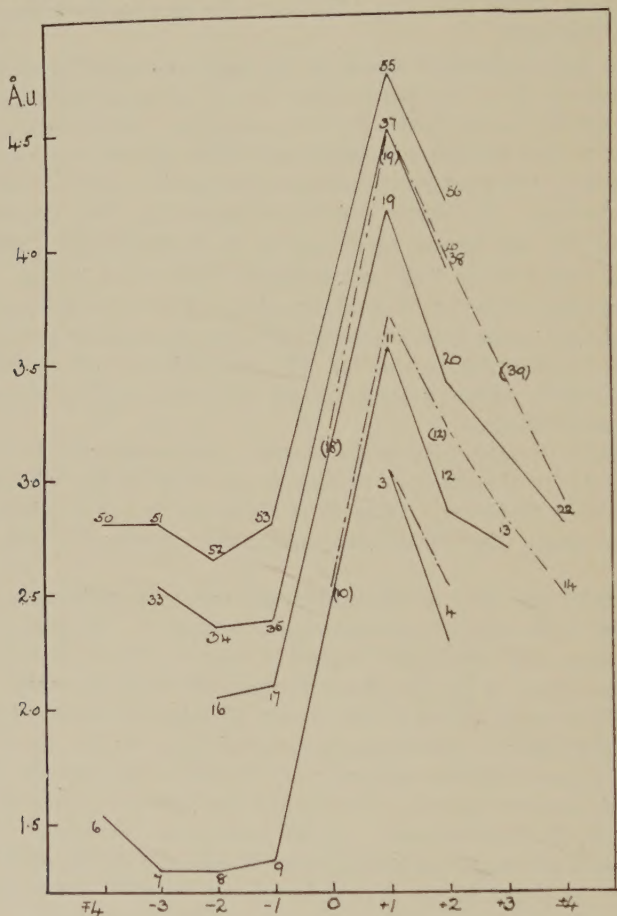


FIG. 2.—“ DIAMETERS ” OF ATOMS (IONS) IN CRYSTALS, RECORDED BY BRAGG, WITH ATOMIC NUMBERS. DOTTED LINES DUE TO DAVEY.

determined solely by the atomic numbers  $N_1$  and  $N_2$  of two neighbouring atoms, and an empirical relation is suggested:

$$d = a \log (N_1 - N_2) + b.$$

It is, indeed, possible to obtain an approximate logarithmic expression for the shape of the descending parts of the Bragg curve (for the first four elements following each peak), but this cannot be of much significance, and it is impossible to retain the hypothesis of constant atomic “radii” in even its useful approximate form if this formula is accepted.



## METHOD 3.—GAS VISCOSITY.

The work of Chapman,<sup>(14)</sup> Rankine,<sup>(15)</sup> and others is well known, and has set this method on a very sound footing. It leads directly to the mean area offered by gaseous molecules in elastic collisions between themselves, and the diameters of the molecules can be obtained if their sphericity is assumed, from the formula

$$\pi d^2 = \frac{0.347 \rho V}{N \eta (1 + S/T)}$$

This only provides atomic data in the case of the monatomic gas. Rankine<sup>(17)</sup> has examined the possibility of connecting the diameter of the atom with the size of its molecule. He has also considered the variations in molecular size in series of compound molecules—for example, the effect of the hydrogen protuberance in the successive hydrides of a series is now clear; but it is not yet possible to estimate the separate atomic sizes.\* Some molecular results are recorded in Figs. 3 to 6; the only atomic diameters are

He, 1.89; Ne, 2.35; Ar, 2.87; Kr, 3.19; Xe, 3.51 (all in Å.U.).

## METHOD 4.—EQUATIONS OF STATE.

The value of the co-volume  $b$  in the Van der Waals equation of state can be obtained for a dozen elements, both from their critical constants and from their behaviour in the gaseous state. Its interpretation rests upon similar hypotheses to those of Method 3, but here the spheres of action are measured, not the mean collision areas, and the reduction from molecular to atomic data is still more uncertain. Chapman's analysis leads to excellent numerical accord in the values of the diameter between the two methods.<sup>(19 & 20)</sup>

Similar calculations have been based upon the form given to the equation of state by Kamerlingh Onnes, and have led to estimates of atomic diameters by Debye,<sup>(21)</sup> Keesom,<sup>(22)</sup> and Zwicky.<sup>(23)</sup> In their work, however, the atomic fields of force are more explicitly considered, and as these are probably known with less certainty than the atomic dimensions, the results are of less value for our present purpose. Zwicky calculates that the diameter of the helium atom, from the observations at low temperature, is 2.78 Å., and at 20°C. it appears to be 2.25 Å.; it is more probable that the thermal motion has been inadequately allowed for in the theory than that the equivalent size changes in this proportion.

Results:

(Chapman) He, 1.96; Ar, 2.85; Kr, 3.14; Xe, 3.42.  
(Pease)<sup>(24)</sup> Ne, 2.37; Ar, 2.93; Kr, 3.15; Xe, 3.43.

## METHOD 5.—COMPRESSIBILITY.

The measurements by Bridgman of the compressibility of the alkali halides have led Richards<sup>(25)</sup> to some important estimates of atomic size. The pressure volume law for the solid salts is found to contain a "co-volume" term  $b$ , from which the sizes of the molecules may be deduced. Further, and with more accuracy, the degree to which contraction occurs as the various chlorides are formed is found to be connected in a simple way with the compressibilities of these salts, and the figures

\* Some progress in this direction is recorded by Lorenz,<sup>(18)</sup> in confirmation of Schroder's law for the addition of atomic volumes, in a considerable number of large molecules.

permit a clear separation of the contraction in the alkali from that in the halogen. Since the usual atomic volume is well known, the volume of the ion is readily obtained. It increases slightly with the size of the ion with which it is combined—e.g., the caesium ion has an equivalent diameter of 3.66 Å.U. in its chloride, 3.69 Å.U. in the bromide, and 3.82 in the iodide. The halogen ions are constant in volume. The results are for equivalent diameters in Ångstrom units :

Cl, 2.8 ; Br, 3.1 ; I, 3.4 ; Li, 2.3-2.6 ; Na, 2.9-3.1 ; K, 3.5-3.7 ;  
Rb, 3.8-3.9 ; Cs, 3.7-3.8.

METHOD 6.—VISCOSITY OF LIQUIDS.

METHOD 7.—VISCOSITY OF SOLUTIONS.

METHOD 8.—DIFFUSION OF IONS. METHOD 9.—MOBILITY OF IONS IN SOLUTIONS.

Jäger<sup>(26)</sup> extended the ideas of the kinetic theory to the viscosity of liquids, considering the molecules so closely packed that the free path was simply the molecular "diameter." The conditions involved in his analysis are best satisfied by mercury, and for this liquid (and this only) the result is of the right order— $d=3.58$  Å.

Measurements of diffusion must lead to dimension data, but at present the only path available to this end is to assume that the diffusing molecule is a sphere, and that it moves against a resistance given by Stokes' law. Einstein's<sup>(27)</sup> use of this idea for the large molecules of sugar, both in their influence on viscosity in solutions and in their diffusion through organic liquids, is probably sound ; its application for small molecules is very doubtful. Surprisingly good results follow, however, at the hands of Lorenz,<sup>(28)</sup> who uses Wogau's figures for the diffusion of alkali atoms through mercury. Smith<sup>(29)</sup> has shown that the ions, and not the atoms, are here being dealt with.

The treatment of the mobility of ions in solution follows a similar path, also first trodden by Lorenz with quantitative success ; but when water is the solvent many special difficulties arise, probably because of the uncertain amounts of hydration. Walden<sup>(30)</sup> has examined a specially long series of solutions in organic liquids, and applied to them a form of Einstein's result—viz.,

$$d = \frac{15.96 \times 10^{-3}}{u\eta}$$

where  $u$  is the velocity of the ion and  $\eta$  the viscosity of the solution. Some of the ionic diameters for solutions in methyl alcohol are :

H, 1.11 ; Cl, 2.49 ; Br, 2.39 ; I, 2.42 ; Li, 4.52 ; Na, 3.48 ; Rb, 2.24 ; Co, 2.22.

These are in descending order of magnitude, and suggest that the smallest ions are most surrounded by attached water molecules. Born's<sup>(31)</sup> able attempt to carry the theory of the electric forces on molecular dipoles into this domain does not yet lead to probable values for the ionic diameters, although the results are now in the right order :

Li, 0.90 ; Na, 1.02 ; K, 1.34 ; Rb, 1.54 ; Cs, 1.66.

#### METHOD 10.

An extension<sup>(32)</sup> of the same ideas to the energy released when a free ion dissolves in water does, however, yield reasonable values. This energy involves the electro-



static field of force of the solvent molecules, and the size of the ion governs the extent to which it enters into this field. It is remarkable that the ionic radius of action as thus specially defined should accord with the usual values. Some results appear in Fig. 3.

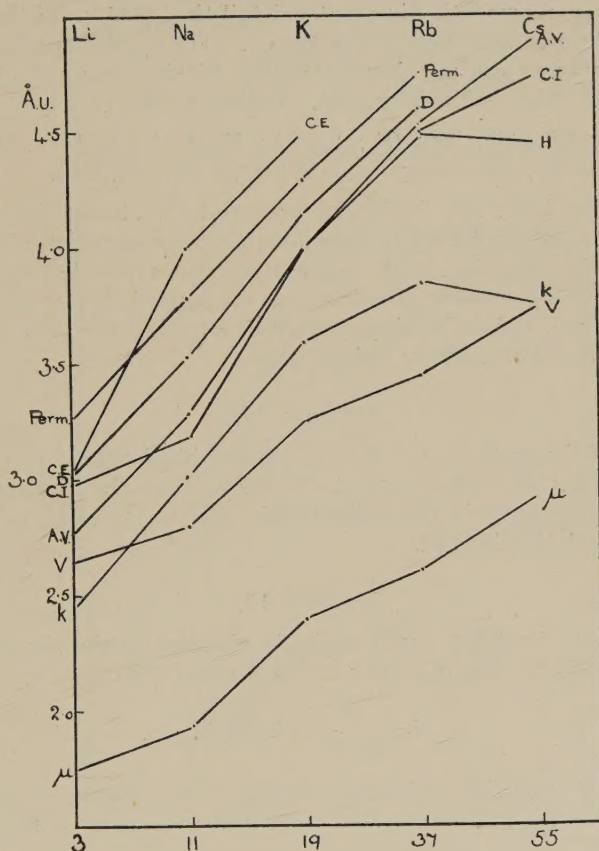


FIG. 3.—ATOMIC DIAMETERS OF GROUP I ELEMENTS.

- C.E. : Crystal element (Hull).  
 C.I. : Crystal ion (Bragg).  
 Perm. : Permutite (Günther-Schulze).  
 D. : Diffusion in Hg (Lorenz).  
 A.V. : Atomic volume—cube root.  
 H. : Hydratation (Born).<sup>(32)</sup>  
 k : Compressibility (Richards).  
 V : Ionisation potential (Saha).  
 μ : Molecular refraction (Wasastjerna).

#### METHOD 11.

The electrostatic theory of crystal structure due to Born<sup>(33)</sup> and Landé, and the contributions of Debye<sup>(34)</sup> towards a more satisfactory electromagnetic theory, lead to values for the ionic radius of action. The former deals with a cubic packing, or, in the form adopted by Bohr,<sup>(35)</sup> with a tetrahedral unit. Consistent values are



only obtained if the positive and negative ions in the molecule are about the same size. Monovalent atoms have been examined by Fajans<sup>(36)</sup> and Herzfeld, divalent by Grimm,<sup>(37)</sup> and in these lengthy calculations the repulsion, according to the inverse ninth power law suggested by Born, is supplemented by a repulsion term of the inverse fifth power, representing in greater detail the influence of the charges in the anion upon those of similar size in the kation. The results are diameters varying in the usual way from one member to another within one group, but all of them much smaller than other methods suggest. Grimm's results are :

F, 1.50 ; Cl, 1.90 ; Br, 2.04 ; I, 2.24 ; Ma, 1.04 ; K, 1.58 ; Rb, 1.92 ;  
Cs, 2.14 ; Mg, 0.78 ; Ca, 1.34 ; Sr, 1.74 ; Ba, 2.14.

It is clear that here, too, the law of force and the atomic size are inextricably mixed at present, and until further experiments on the variation of compressibility, or of crystal lattice-distances, with temperature, are available this method cannot give reliable information about atomic sizes. It is much better used as a guide to atomic fields of force, and, in particular, may soon lead to an estimate of the relative contributions of the Born and the Debye forces.

#### METHOD 12.

The study of the scattering of X-rays has led, incidentally, to several estimates of atomic diameters. The best appears to be a result for the diameters of the orbits of the outermost electrons in the sodium and chlorine ions, due to W. L. Bragg<sup>(38)</sup> and others : Na=1.40, Cl=2.90.

#### METHOD 13.

Bohr's theory of atomic structure leads directly to the size of the hydrogen atom, and to no other. The diameter of the electron orbit is

$$d = \frac{h^2}{2\pi^2 m e^2} = 1.074 \text{ \AA}.$$

The diameter of the positive helium ion should be one quarter of this. Landé's<sup>(39)</sup> calculations of the rare gas atomic structures and sizes rests on bases now believed to be faulty.

#### METHOD 14.—IONISATION POTENTIAL.

A simple description of the mechanism of ionisation has been suggested by Eve<sup>(40)</sup> and by Saha.<sup>(41)</sup> The detached electron is assumed to move in a circular orbit, and the work required to remove it is inversely proportional to the orbit radius, if the influence of other electrons is neglected. Eve showed that the present meagre data suggest that the factor of proportion varies from group to group among the elements in a regular manner. The figure obtained by the method of Saha for the atomic diameter is a little low for Na, K, etc., lower for Ca, Ba, etc., and much too low for the rare gases, which also suggests that an allowance is required for the other electrons in the outer ring. Some results are shown in the graphs ; others are :

Zu, 1.54 ; Cd, 1.61 ; Hg, 1.39 ; Tl, 1.98 ; Pb, 1.82 ; As, 1.25 ;  
Pb, 1.10 ; He, 0.57 ; Ne, 0.90 ; Ar, 1.12.



## METHOD 15.

The refractive indices of gases and of aqueous solutions have been examined independently by Heydweiller<sup>(42)</sup> and by Wasastjerna.<sup>(43)</sup> The former used Kelvin's idea of the electron displacement within a sphere of positive electricity, and the latter applies a similar idea to the Bohr atom. It is assumed that the electric moment of the molecule is proportional to the volume of the atom; and the estimates of atomic diameters—which are of the right order—refer to an equivalent sphere, as

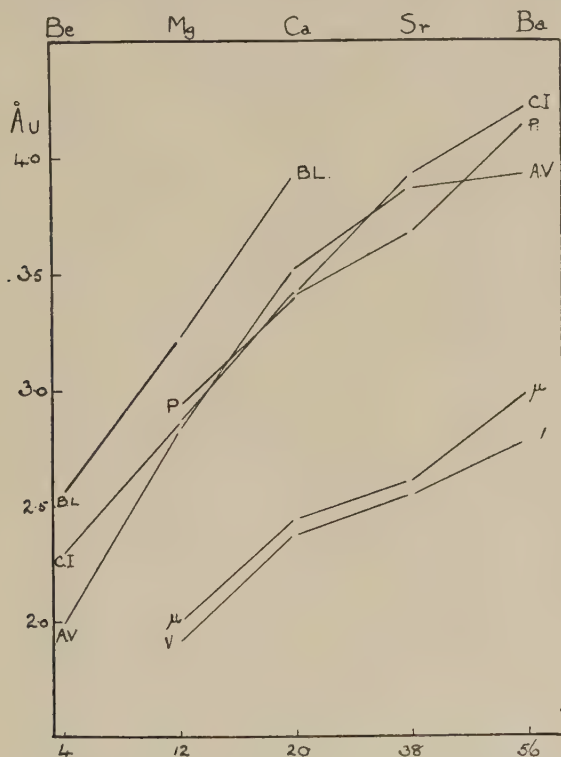


FIG. 4.—ATOMIC DIAMETERS OF GROUP II ELEMENTS.

B-L. : Crystal lattice theory (Born-Landé).

C.I. : Crystal ion (Bragg).

P. : Permutite (Günther-Schulze).

A.V. : Atomic volume—cube root.

$\mu$  : Molecular refraction (Heydweiller).

V : Ionisation potential (Saha).

in the Mosotti theory, of electric moment equal to that of the real atom. For dilute solutions the effect is an additive one for the ions concerned, and hence the ionic "diameter" is determined. The results are shown in Figs. 3 to 6. The agreement of these figures with other estimates has been shown indirectly by Calthrop,<sup>(44)</sup> who has compared the values of  $\mu-1$  with the cubes of Bragg's figures, and shown that their ratio is a constant in any one group.



## METHODS 15 AND 16.—BAND SPECTRA : CHEMICAL CONSTANT.

Molecular moments of inertia have been very satisfactorily calculated<sup>(47)</sup> from the infra-red spectra of several gases ( $H_2$ ,  $O_2$ ,  $N_2$ ,  $H_2O$ ,  $HCl$ , etc.), and confirmed by Kratzer's<sup>(45)</sup> application of a theory of the fine structure of the bands. The same is true of the values deduced by Langen<sup>(46)</sup> from the values of the chemical constant, based on a statistical sum of molecular energies, though here the experimental

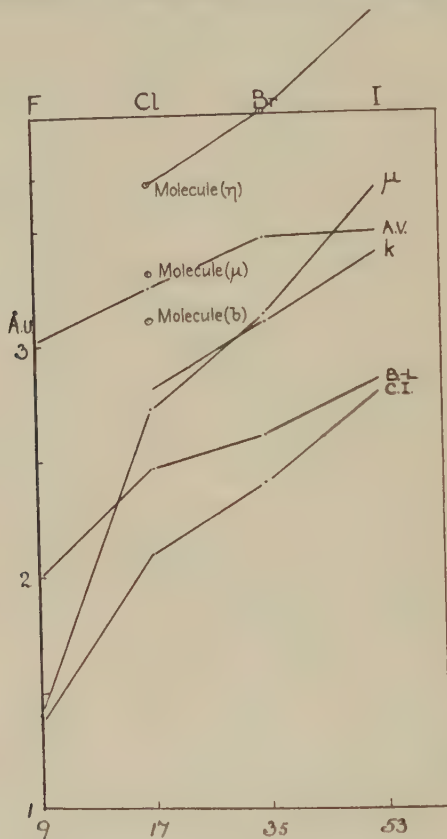


FIG. 5.—ATOMIC DIAMETERS OF GROUP VII ELEMENTS.

$\mu$  : Molecular refraction (Heydweiller).

$k$  : Compressibility (Richards).

B.-L. : Crystal lattice theory (Born-Landé).

C.I. : Crystal ion (Bragg).

A.V. : Atomic volume—cube root.

results are much less accurate. In both cases the molecular diameter appears to be smaller than is given by other methods.

## METHOD 17.

It is probable that the amount of optical rotation of a molecule may be connected with the ionic dimensions. It has been pointed out by Brauns<sup>(48)</sup> that the

effect of replacing one halogen by another, in various glucose and xylose compounds, is to alter the molecular rotation by an amount proportional to the difference between the atomic diameters of the two halogens. It is suggested that the dimension of the halogen atoms determines the amount of asymmetry in the molecule, and this determines the rotation. The suggestion has not been further applied.

#### METHOD 18.—MOLECULAR FILMS.

Many estimates of the dimensions of large organic molecules have been made

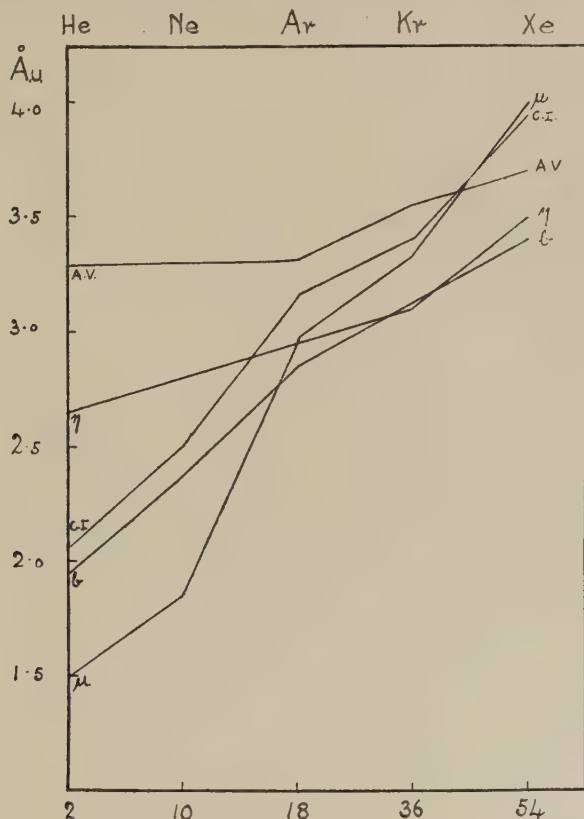


FIG. 6.—ATOMIC DIAMETERS OF RARE GASES.

- $\mu$  : Refractive index (Wasastjerna).  
 b : Equations of state (Chapman and others).  
 C.I. : "Crystal ion" (Davey).  
 $\eta$  : Viscosity (Rankine).  
 A.V. : Atomic volume—cube root.

by the film method, notably by Pockels and Rayleigh in the last century, and by Langmuir,<sup>(49)</sup> Harkins<sup>(50)</sup> and Hardy<sup>(51)</sup> recently. The available methods are at present restricted to these large molecules, and, as comparison with the atomic dimensions is impossible, it is only necessary here to say that they in no way conflict



with the other data. For instance, the dimensions of the molecule of sodium oleate, as carefully estimated from surface tension experiments by du Noüy,<sup>(52)</sup> are, in three directions, 6.64 Å.U., 7.56 and 12.30 Å.U.

One set of measurements on inorganic substances deserves mention, that by Devaux<sup>(53)</sup> (repeated by Marcellin).<sup>(54)</sup> It was shown that unimolecular films of several sulphides and of Ag I could be obtained. For CnS the thickness was 2.7-3.1 Å., which is in good accord with the results of later methods.

#### METHOD 19.—MAGNETIC THEORIES.

Langevin's theory of diamagnetism leads to a connexion between the susceptibility and the total area of electron orbits within the atom. This latter quantity can therefore be deduced from experimental data, and if the number of circulating electrons is known the diameters of their orbits may be estimated. Pauli<sup>(55)</sup> (and before him Cabrera) have not found that the results are good, but the deductions made by Young<sup>(56)</sup> are of the right order for elements. In calculating the contribution of each orbit to the total diamagnetism, Young used the Bohr ratios for the orbital radii, in one case, and replaced the shells of the Langmuir atom by equivalent orbits in a second case; the results are similar in both cases.

#### METHOD 20.—ELECTRON STREAM IN A GAS.

The number of electrons which encounter molecules in passing through a gas is a measure of the molecular size.<sup>(57)</sup> Some gaseous molecules,<sup>(58)</sup> as O<sub>2</sub> and CO<sub>2</sub>, appear to possess a special affinity for electrons which renders the calculation of their size impossible. Further, for the gases chiefly studied, He, Ne, H<sub>2</sub>, N<sub>2</sub>, the measured size depends upon the speed of the electrons, and reaches a permanent maximum value as this speed falls.<sup>(59 & 60)</sup> In the case of He and Ne and N<sub>2</sub> this final value is in fair accord with the results from viscosity measurements. For Kr and Xe Ramsauer<sup>(61)</sup> concludes that the effective atomic cross-section increased from one seventh of the expected value up to five times this value, as the velocities of the electron stream rose from 0.7 volts to 10 volts. Deductions of atomic size are therefore at present impossible.

The bombardment of molecules by a stream of silver atoms has not yet yielded good results on this point, by reason of the great experimental difficulties.

#### METHOD 21.

Some interesting calculations have been made by Günther-Schulze<sup>(63)</sup> after measuring the densities of different forms of permutite. In this complex and artificial silicate one ion may be replaced by another in regular order, and the consequent changes in molecular volume are a measure of the differences in the volumes of the substituted ions.

Results :

Li, 3.26 ; Na, 3.78 ; K, 4.30 ; Rb, 4.74 ; Mg, 2.92 ; Ca, 3.38 ;  
Sr, 3.66 ; Ba, 4.14 ; Ag, 3.56.

## METHOD 22.

Lindemann<sup>(64)</sup> has suggested that a solid melts when the amplitude of its heat vibrations is such that neighbouring atoms collide, and this leads to good results for many metals.

## CONCLUSION.

The chief numerical results are collected and shown in Figs. 3 to 6. The accord

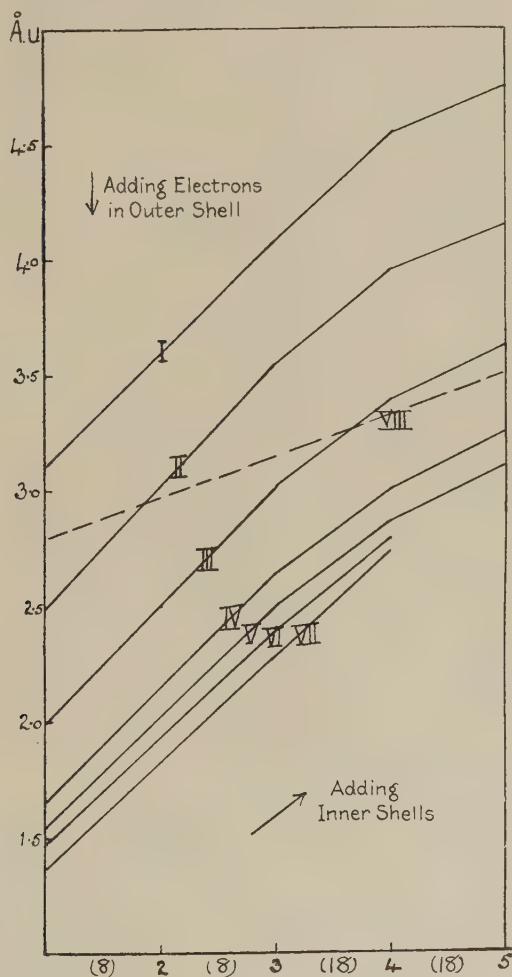


FIG. 7.—MEAN "ATOMIC DIAMETERS" FOR ELEMENTS OF ALL GROUPS.

between the different methods is, on the whole, very promising. Finally, in Fig. 7, a rough mean has been taken from the preceding figures, and the variation in size throughout the groups is presented in a way which shows both the increase in size as the number of electron "rings" or "shells" is increased, and also the contraction which goes on as the number of electrons in the outer ring is increased. The figures,



for the electronegative elements rest necessarily too much upon two methods only ; and they do not settle the most interesting question—whether the contraction continues up to the seventh group, as shown, or whether the increase which is striking in the 8th group really commences with the 7th or the 6th. There is evidently a parallelism among the groups ; and the effect of adding an inner shell is an increase in diameter of, roughly, 0.5 Å. in every case.

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## DISCUSSION.

Prof. A. M. TYNDALL: The Paper is a very useful summary of experimental data. At the same time it would be more valuable if an account of the recent important theoretical work of Lennard-Jones could be incorporated in it. On modern theories one must emphasize the difference between atomic and ionic sizes. For instance, the position of sodium in a table of the dimensions of the various elements is different according to whether one is thinking of the uncharged atom or of the positive ion. The atomic volume results refer to the former, and Wasastjerna's to the latter. Consequently, therefore, the "average" values given in Fig. 7 can hardly be regarded as having a real physical significance.

Dr. J. H. VINCENT said that in Fig. 1 the straight line representing the rare earth elements is marked with a reference to the element 72, which thus occurs twice. It would be better to substitute "71" in this figure. The graph could be more conveniently drawn to logarithmic scales; this plan would facilitate certain adjustments in the case of the ordinates, and in the case of the abscissæ (valencies) it would obviate the necessity for an arbitrary change of scale for the long periods. The negative valencies could be represented by the logarithms of the valency numbers plotted leftwards from the origin.

Mr. J. E. CALTHROP: In such an extensive list of references, I think some mention might be made of a Paper on "Molecular Diameters," by H. Sirk (Phil. Mag., 49, pp. 708-711, 1925). The diameters for a number of substances are calculated from latent heats of vaporisation, and the values obtained appear to be about 1.37 times the corresponding values derived from the Kinetic theory of gases. The result for Argon is a diameter of 3.6Å. in good agreement with 3.8Å. found from X-ray measurements on crystal Argon by Simon and Cl. v. Simson. Both these values are greater than the value given in Fig. 7 of Mr. Lunnion's Paper.



Prof. T. H. LABY said that, since modern views of atomic structure preclude us from regarding the atom as an elastic sphere, the diameter measured by each method is really a different quantity: the differences between the results obtained represent real physical differences, and not experimental errors. X-ray measurements are accurate to 0.1 per cent., and even observations on gas molecules give an error less than the differences between the results obtained by different methods. It is, therefore, incorrect to take a mean value of all the results.

Dr. GEOFFREY MARTIN: This Paper appeals to chemists as well as to physicists. In fact, many of the Papers read before the Society are of considerable chemical interest, and I think it rather a pity that the dates of many chemical functions overlap those of physical meetings, and make it a difficult matter for anyone to attend both series of meetings, especially as I think that chemists and physicists should co-operate together more than they do. Recently I have been carrying out researches on the fine grinding of quartz sand. I have measured the weights, diameters and surfaces of both very coarse and very fine particles, and have proved that they possess the same average shape. One curious practical application of molecular dimensions is that they can be utilised for determining the mechanical efficiency of grinding machinery in absolute terms. One imagines the power to be reduced to molecular dimensions. Then the work theoretically required to do this is the total heat of volatilization. By assuming a straight line law and measuring the power absorbed in the actual grinding operations, I have shown that the efficiency of the tube mill is only about 1/15th per cent.

When reading the Paper I was reminded of work that I carried out as a young man over 20 years ago. The periodic table of Mendeleef was used as a base, and from each element an ordinate was erected proportional to the chemical attraction it possessed for any one atomic species (as measured by the heat of formation or decomposition of its chemical compounds with that atomic species). In that way a series of surfaces was obtained, one peculiar to and characteristic of each elementary substance. It was proved that chemically similar elements produced similarly shaped surfaces, and therefore two elements were chemically similar when they exerted, not equal, but *proportional* forces on the same elementary atoms. Also that when any element (say iron) entered a different valency state it produced a different surface. So that when an element changed its chemical forces it changed its chemical characteristics. Consequently the properties, both chemical and physical, of an element were decided entirely by the forces it exerted. Two elements would possess the same properties and could replace each other (no matter what their atomic weights were) if they exerted the same forces.

Dr. P. E. SHAW (communicated): In Papers before the Physical Society (1900) and Royal Society (1905) I showed the possibility of setting two surfaces at the small distance apart of  $0.5 \times 10^{-7}$  mm. These distances, which were measured by the electric micrometer and telephone, are little, if any, more than the atomic dimensions of the metals of which the surfaces are made. I have not been able to follow up the curious effects audible in the telephone when the electric discharge occurred between the surfaces, which had been maintained as some very small P.D. The sounds heard were peculiar for certain metals, notably lead. It seems to me that some use might be made in present-day sub-atomic research of this method of obtaining a very small gap or slit.

AUTHOR'S reply: It is clear that a different atomic dimension is measured by each of the methods referred to in this Paper, and that it would be wrong in principle to claim any absolute significance for the lines of Fig. 7. Nevertheless the surprising similarity between the result of different theories makes it very probable that the diagram is on sound lines in its suggestions as to the variation of size from atom to atom within each group, and from group to group; and its only purpose is to show the trend of these variations. The Paper affords evidence that the variations are similar whether ions or neutral atoms are considered. A discussion of the exact meaning of "diameter" was purposely excluded from this brief survey, and for this reference must be made, for example, to the Papers of Lennard-Jones (Proc. Roy. Soc., 109, 476, 1925, and previous Papers).

## XIV.—ON EDGE-TONES (I).

By W. E. BENTON, *B.Sc.*, University of Birmingham.*(Communicated by PROF. S. W. J. SMITH, F.R.S.)*

## ABSTRACT.

An edge-tone is heard when a stream of air issuing from a slit or hole strikes a sharp edge, or surface bounded by sharp edges. A brief description is given of previous work, and it is shown that the eddies which give rise to edge-tones conform to a simple Kármán vortex-system. On the assumptions (1) that the distance  $a$  from the edge to the slit is always equal to  $l$ , the distance between two eddies in the same row, and (2) that tone is destroyed when the edge—when moved across the jet towards still air—crosses the line of eddy centres, one can measure  $h/l$ , where  $h$  is the separation of the eddy-rows, directly from measurements of the boundaries for tone. From the experiments it is found that at low pressures and with wide slits  $h/l$ , for air,  $=0.276$ , which may be compared with v. Kármán's prediction of 0.283 for an infinite system in a perfect fluid.

If the edge is moved towards the slit,  $h$ , the separation of the eddy-rows, must decrease proportionally. The experiments show that when the eddies are formed very close to the edges of the slit, and therefore in a field of high velocity-gradient at right angles to the direction of motion, they are deflected towards the middle, or principal, plane of the jet. The amount of this deflection increases very rapidly as  $a$  approaches  $a_0$ , at which distance tone can only be obtained when the edge lies in the principal plane. The experiments show that with wide slits, when  $a=a_0$ , then  $l=a_0$ ;  $h=0.67a$ , where  $d$  is the width of the slit. The minimum distance for tone,  $a_0$ , varies with the velocity  $v$ , and the width of the slit.

The results suggest an equation of dynamic similarity:—

$$B \left( \frac{\nu}{vd} \right) = \left( \frac{a_0}{d} \right)^2 - 1.50$$

where  $B$  is a number (about 2,000 for air) and  $\nu$  is the coefficient of kinematic viscosity. By considering the acceleration that produces the deflection, an expression of somewhat similar form can be obtained theoretically. The tonal boundaries in the region of simple tone approach two straight-line asymptotes, equally inclined to the principal plane, which converge at a point near the plane of the slit. If  $\bar{a}$  and  $\bar{a}_0$  denote the distance of the edge and the minimum distance for tone respectively from 0, the total separation,  $y$ , of the two boundaries at any distance  $\bar{a}$  is given by the equation:—

$$y = \frac{h}{l} \bar{a} - \frac{h}{l} \bar{a}_0 e^{-m^2(\bar{a}^2 - \bar{a}_0^2)}$$

where  $1/m$  is approximately equal to  $\bar{a}$ , when the slit is very wide. The measurements of the frequency of the tone and the deductions made from them will form the subject of a subsequent communication.

## A. INTRODUCTION.

THE natural frequency of vibration of a body of air contained in a pipe or resonator may be excited by blowing gently across the aperture—in the case of a pipe, across the open end. It was formerly believed that the action of the air-jet was similar to that of a clock-escapement, the motion depending essentially on the assistance of the air contained within the resonator. Recently it has been established that the origin and maintenance of the tone of a flue organ-pipe are due to the natural vibration, about the rigid upper lip, of the thin stream of air issuing from the throat (Kernspalt). The investigation of this natural motion, when remote from the influence of a resonator, comprises the study of edge-tones. The general characteristics of edge-tones were first described by Sondhauss, and his results have been repeated and extended by Hensen, Weerth, Wachsmuth and Kreis. They noted



that the edge must be parallel to the plane and to the direction of length of the slit, and should be in the middle of the air-stream, in what we may call the principal plane of the jet.

When the edge is very close to the slit, no tone is obtained. At a distance  $a_0$  (dependent on the nature of the gas, the width of the slit and on the velocity of the jet) a note suddenly appears, of a pitch dependent principally upon the velocity and the value of  $a_0$ . As the distance is increased the pitch of the note falls steadily until at a distance  $a_1$  the note suddenly "jumps" to its octave. As the distance is still further increased the frequency again falls, until at a distance  $a_2$  it jumps suddenly to the "fifth" above. Subsequently, at  $a_3$ , there occurs a jump of one-fourth, and under certain conditions six or eight of these breaks may be detected. In 1912, W. König, using Gölner's experimental work at Rostock, suggested that the frequency  $n$  of an edge-tone is given by the formula

$$n = \frac{vi}{2a}$$

where  $v$  is the total quantity of air per second, leaving each sq. cm. of the slit;  $a$  is the distance of the edge from the slit, and

from	$a_0$ to $a_1$	$i=1$
	$a_1$ to $a_2$	$i=2$
	$a_2$ to $a_3$	$i=3$ , etc.

König tentatively suggested that

$$a_0 = \frac{a_1}{2} = \frac{a_2}{3} = \frac{a_3}{4}, \text{ etc.}$$

The difficulty of measuring air-velocities led Schmidtke to prefer the use of a jet of water, issuing into water, and his observations show that König's formula is approximately true for water.

#### B. APPARATUS.

In commencing the present work, it was decided to preserve the following conditions:—

- (1) The air-jet to issue from a region of still air.
- (2) The jet to leave the slit perfectly smoothly.
- (3) The jet to be normal to the plane of the slit.
- (4) To avoid possible distortion of the streamlines by allowing the presence of no large object near the jet.
- (5) The edge to be rigid and sharp.
- (6) The approach to the slit, from inside, to be streamlined, so that the jet undergoes no contraction after leaving the slit.
- (7) The air-pressure and the slit-width to be adjustable.
- (8) The edge to be able to move in directions parallel and perpendicular to the central (or principal) plane of the jet.

The apparatus shown in Fig. 1 adequately fulfils these conditions. Compressed air is admitted through the tap  $A$  into the wind-chest  $B$ . The turbulence produced at the top is destroyed by passing the air through a sheet of fine wire gauze at  $C$ .

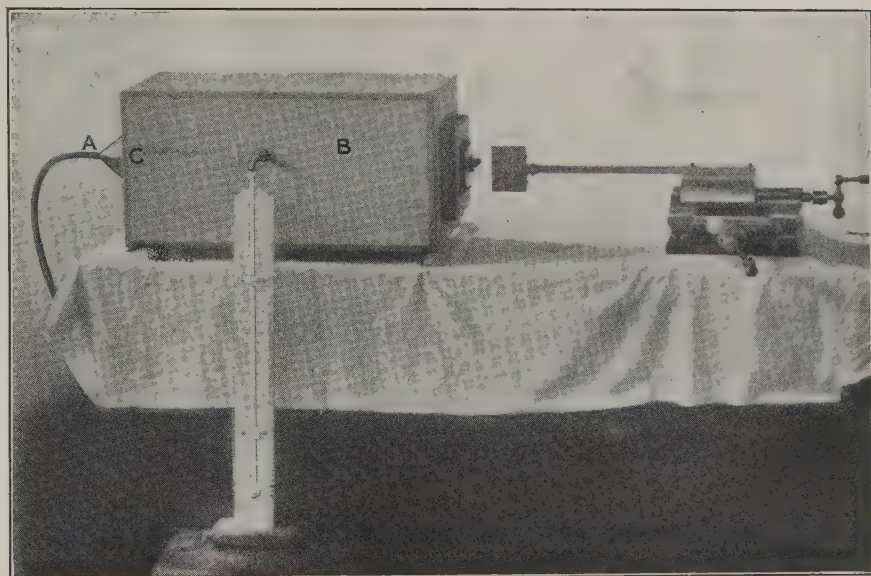


FIG. 1.





To prevent the formation of any central stream of rapidly moving air, the centre of the sheet is blocked out with solder. The cross-section of the box (900 sq. cm.) is so great compared with that of the slit—seldom more than 1 sq. cm.—that the air in the box may be considered at rest. The vertical water manometer, introduced mid-way in the length of the box, may therefore be considered to read the actual excess pressure to which the velocity of the jet is due. The corners of the box on the forward face are covered inside by a metal cone which prevents the formation of any “dead-space” in which large eddies might easily arise. All other edges are similarly removed, so that the air approaches the slit, formed between two polished brass edges, in easy streamline motion. The inner edges of the slit are bevelled, so that eventually the air leaves normally to the plane of the slit. The length of the slit is 10 cm.\* The edge to be introduced into the air-stream is of mild steel, bounded by two polished plane faces enclosing an angle of about  $5^\circ$ , mounted at the end of a long iron bar (1 ft. in length by  $\frac{1}{2}$  in. square), fixed rigidly to the movement carriage. It was considered necessary to remove so large a mass as that of the movement carriage from the vicinity of the jet, and the bar supporting the edge, though long, was strong enough to resist vibration. The movement carriage, which was firmly fixed to the table, enabled the edge to be moved in directions perpendicular and parallel to the principal plane of the jet, with an accuracy of movement of about 0.001 cm. in either direction over distances of about 1 cm. Very small distances, such as those occurring in the tonal-boundary measurements, could be estimated to 0.00025 cm. The total possible movement was some 20 cm. perpendicular to, and 10 cm. parallel to, the principal plane of the jet.

This process of removing all sources of complication and error, however, also removed the most interesting characteristic of the edge-tones studied by Wachsmuth, namely, the succession of breaks in the tone as the distance of the edge from the slit increases. Using a narrow slit, and moving along the principal plane, a bright clear tone appears at a distance  $a=a_0$ . This undergoes small variations in quality as the distance increases, the bright octave quality changing gradually to an almost pure tone, and thence to an unpleasant nasal sound. The nasality increases rapidly as  $a$  approaches a value  $a_1$ , when a harsh discordance suddenly appears. Here the former tone can be recovered, somewhat thinner in quality, by moving the edge slightly across the jet. In the present experiments measurements have been confined to the simple region of comparatively pure tone.

### C. THEORY.

Wachsmuth's “Schlierenbilder” show that in the first interval ( $a_0 < a < a_1$ ) an eddy on the left-hand side of the jet is about to pass the edge when another on the same side is being formed at the slit, while on the right-hand side a third eddy lies half-way between the slit and the edge. The period of oscillation is the interval of time between the release of two successive eddies on the same side of the jet—i.e., for this particular state the period is the time taken for the eddy to move from the slit to the edge. Now, if the eddies were very small, and if the air-stream could be considered as a sharply-defined belt of moving air, one might assume that an eddy moved as a “roller” in contact with a moving belt, having at any instant a point in contact with the belt moving with velocity  $v$ , and one point furthest from the

\* Wachsmuth used a slit 1 cm. long. Hensen's slit was 4 cm. long.



belt, momentarily at rest. The velocity of the eddy would then be one-half the velocity of the belt, and the time taken to traverse the distance  $a$  would be  $2a/v$ . The frequency of vibration of the air-stream about the edge would therefore be given by

$$n = \frac{v}{2a}$$

which is König's formula.

A wind-tone of any kind is the acoustical result of the formation of two parallel rows of eddies (or of eddy-rings lying on two coaxial cylinders) advancing with uniform velocity.

Th. von Kármán considered the perfect case of two infinite parallel rows of rectilinear vortices in which the senses of rotation of eddies of the same row are like, of different rows unlike. He showed that there is only one possible arrangement for such a system in a perfect fluid to move forward unchanged. The eddies of one row must be placed alternately with respect to those of the other, and the ratio of  $h$ , the distance between the two rows, to  $l$ , the distance between two adjacent eddies in the same row, must satisfy the equation

$$\cosh\left(\frac{h}{l}\pi\right) = \sqrt{2},$$

$$\text{i.e.,} \quad \frac{h}{l} = 0.283 \dots$$

v. Kármán and Rubach made a few experiments with water models and found from photographs 0.305 and 0.280 for values of  $\frac{h}{l}$ .

The system of eddies that gives rise to edge-tones differs from this ideal case in two ways, for it is supported against frictional destruction by a central belt of high velocity, and the edge in some way is absolutely necessary to the formation of the eddies. Instead of two parallel rows of eddies infinite in both directions, one has a system infinite in one direction only, with a rigid barrier placed between the rows extending to within the distance  $l$  of the source. This interval between the slit and the edge may be termed the free space of the system. At any moment each of the three eddies existing in the free space must move with a resultant velocity due to the other two eddies, and the deformation of the system which would inevitably result in time from this motion is checked by the intervention of the edge which separates the members of one row from those of the other, and forces them to continue a uniform progress. The action of the edge-wall on an eddy after passing the edge is such that the normal component of velocity at the wall is zero. If a new eddy were introduced of equal strength, but of opposite sense of rotation, in the position of the optical image of the first eddy with respect to the wall, one could remove the wall without affecting the motion of the fluid. Hence we could hypothetically do away with the edge, if we introduced one of these images for every eddy that had passed the edge. The total effect of such a substitution would be two eddy systems superimposed on the same parallels, and both infinite in one direction only, one system, however, being laterally inverted with respect to the other, and having its origin displaced by the system-interval  $l$  in the direction of motion.

That such a system has some peculiar stability of its own is evidenced by its occurrence in experiment in the working of that useful little instrument the bird-call (Vogelruf, Jageruf), and also in the formation of the tones produced by the passage of air through tubes of pressed metal strip, recently observed by Cermak.

In the bird-call a stream of air passes successively through two circular holes in thin parallel metal plates. The second hole traversed by the air should be slightly larger than the first, and its centre must lie on a line drawn perpendicular to the plane and through the centre of the first hole—i.e., on the axis of the system. The first hole alone would tend to produce an unstable system of eddy-rings, the axes of rotation of the rings lying on two cylinders of diameters slightly greater and slightly less than the diameter of the first hole.\* The second hole produces a similar system of eddy-rings with their axes on the same cylinders, and the combined formation is stable when the origin of the second system is displaced a distance  $l$  from that of the first, the two systems being laterally inverted with respect to each other. In most bird-calls the space between the plates is enclosed, producing a natural resonator, which exerts an action upon the wind-tone similar to that of an organ-pipe upon the edge-tones produced at the mouth.

#### D. MEASUREMENT OF $\frac{h}{l}$ .

In order to measure  $\frac{h}{l}$ , v. Kármán and Rubach photographed the eddies produced in a current of water behind a stationary plate, and conversely behind a moving plate in still water. In air, both the frequency of production and the velocity of translation of the eddies are usually very high, and Wachsmuth's photographs show that even when the air-jet (loaded with ether-vapour to render it refrangible) is photographed, the eddies do not clearly appear, since they are largely formed of entrained air, which does not differ optically from the surrounding medium. From a consideration of the nature of the eddy-system, a very simple method of measuring  $\frac{h}{l}$  was devised. Wachsmuth and Hensen both noticed that when the edge was moved across the air-streams changes occurred in the frequency of the tone, and also a boundary was reached at which all tone vanished. With the present apparatus the lateral boundaries are very sharply defined. With a narrow slit a position can be found from which a lateral movement of 0.0005 cm. will completely extinguish a clear bright tone. The least turbulence in the jet spoils this definition completely. v. Kármán's work readily suggests an explanation.

Consider the edge at some distance  $a$  from the slit (Fig. 2). Then for stability we may assume that the eddy-centres move on two lines  $AB$ ,  $CD$ , each distant  $\frac{1}{2} \frac{h}{l} \cdot a$  from the principal plane. If the edge is moved across the stream towards  $AB$ , a point will be reached when an eddy on that line will be caught by the edge and deflected to the side  $CD$ . The tone cannot then exist. Assume for simplicity that this point is on the path traversed by the eddy-centre. When the edge reaches either  $AB$  or  $CD$ , the tone will be destroyed. If  $a$  is changed, the total lateral move-

\* This system can be rendered stable by employing a sharply cut hole in a thick plate (Kohlrausch).





minimum value characteristic of the slit-width being attained at low pressure. For very wide slits  $\frac{h}{l}$  for air attains a minimum value of 0.276 independent of the slit-width. It may be questioned whether these numbers are really values of  $\frac{h}{l}$ . The reasoning was based on the assumptions that (1)  $a=l$ , (2) that the point of disappearance of the tone occurs when the edge reaches the line of eddy-centres. The diagrams themselves show that one must substitute a linear relation

$$a=l+\varphi(p,d)$$

where  $\varphi$  is some function for the simpler equation

$$a=l$$

The second assumption has no experimental support.

TABLE I.

$d$	Pressure in cm. of water	$\frac{h}{l}$
0.010 cm.	1.01	0.50
	1.98	0.515
0.0365 cm.	0.10	0.32
	0.19	0.33
	0.68	0.35
0.077 cm.	0.34	0.32
	0.62	0.32
0.104 cm.	0.38	0.30
	0.63	0.31
0.132 cm.	0.25	0.285
	0.45	0.309
0.148 cm.	0.25	0.276
	0.39	0.287
0.188 cm.	0.21	0.276

#### E. DETERMINATION OF $a_0$ .

In Fig. 9  $PC$  represents the minimum distance for tone,  $a_0$ .  $O$  may be called the origin and  $P$  the pole of the system. An increase of pressure diminishes  $PC$ . Fig. 4 represents the change of  $a_0$  with pressure for different slit-widths. These curves are not hyperbolæ. In each experiment it was found that a small minimum pressure  $p_0$  existed, below which no tone however faint could be obtained.\* As the pressure approaches  $p_0$ ,  $a_0$  increases very rapidly, and the tones become so faint and so low in pitch that the values of  $a_0$  are difficult to obtain.  $p_0$  is usually about 0.2 cm. of water, and apparently depends on the slit-width, and possibly on the weather conditions. It may represent a small difference of humidity between the

\* Sondhauss said in 1854: "Below a certain pressure, no tone could be heard."



interior and exterior of the wind-chest.\* Fig. 5 shows the relation between  $\frac{1}{\sqrt{p-p_0}}$  and  $a_0$ . Each curve when produced cuts the axis  $a_0=0$  at some value  $\frac{1}{\sqrt{p-p_0}}=-f$  and the axis  $\frac{1}{\sqrt{p-p_0}}=0$ , at some value  $a_0=A$ .

Fig. 6 shows the relation between

$$\sqrt{\frac{1}{\sqrt{p-p_0}}+f} \text{ and } a_0.$$

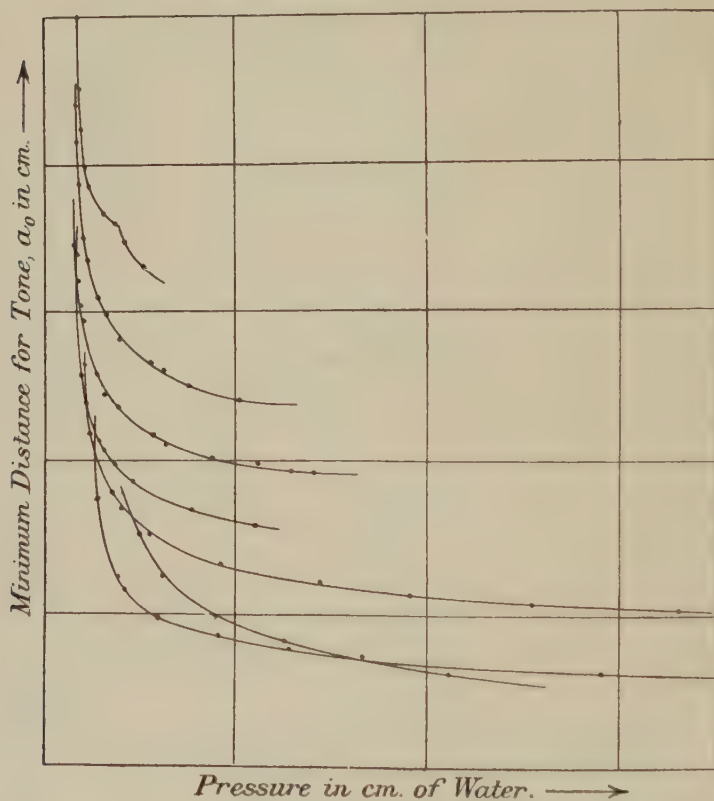


FIG. 4.

Air leaving a slit without resistance under simple adiabatic expansion from a pressure  $P_1$  to a pressure  $P_0$  should attain a velocity  $\bar{v}$  given by

$$\bar{v}^2 = \frac{2\gamma}{\gamma-1} \cdot \frac{P_1}{\rho_1} \left\{ 1 - \left( \frac{P_0}{P_1} \right)^{\frac{\gamma-1}{\gamma}} \right\}$$

where  $\gamma$  is the ratio of the specific heats  $\frac{C_p}{C_v}$ , and  $\rho_1$  is the initial value of the density.

\*  $p_0^2 d$  is approximately constant, where  $d$  is the width of the slit.

For the present purposes, where  $P_1$  is only very slightly greater than  $P_0$  ( $\frac{P_1}{P_0} \approx 1.001$ ) the equation may be simplified. If the manometer records a difference in level  $H$  of liquid of density  $\rho_m$ , we have

$$P_1 = P_0 + \rho_m g H$$

and

$$\bar{v}^2 \approx 2 \frac{\rho_m}{\rho_0} g H$$

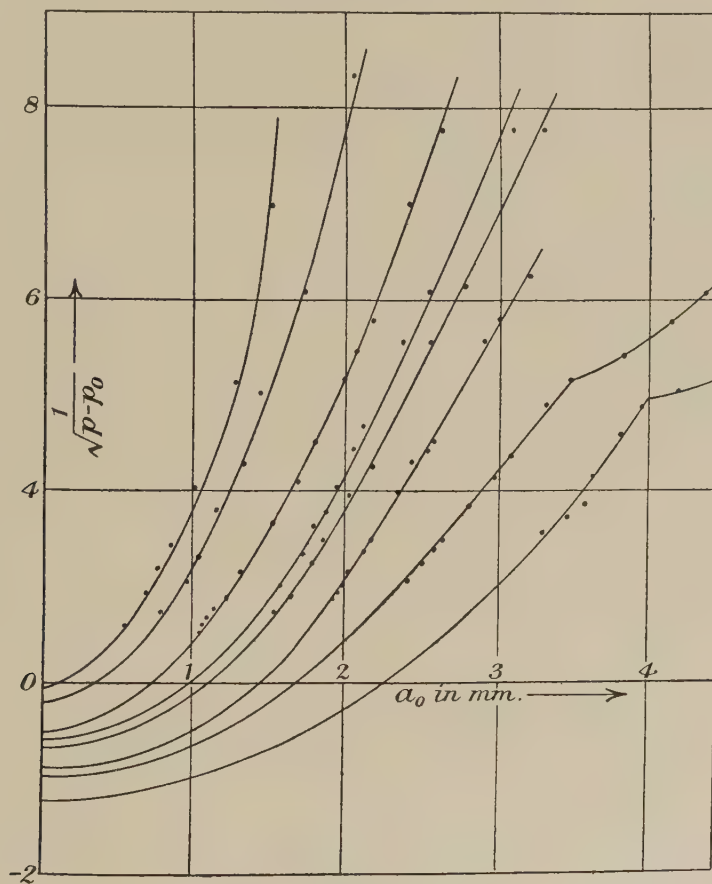


FIG. 5.

For a water manometer at  $0^\circ\text{C.}$  and air initially at the same temperature, we have numerically in c.g.s. units

$$\bar{v} \approx 1232 \sqrt{H}$$

In these experiments the air left a slit formed between polished brass surfaces, the approach to which was stream-lined, and under such conditions it was hoped that there could be no great error in the assumption

$$\sqrt{p-p_0} = v,$$

where  $v$  is a quantity proportional to  $\bar{v}$ .

The quantity  $f$  appears to have no direct physical significance. The length  $A$  however, when plotted against the slit-width  $d$ , gave a straight line passing through

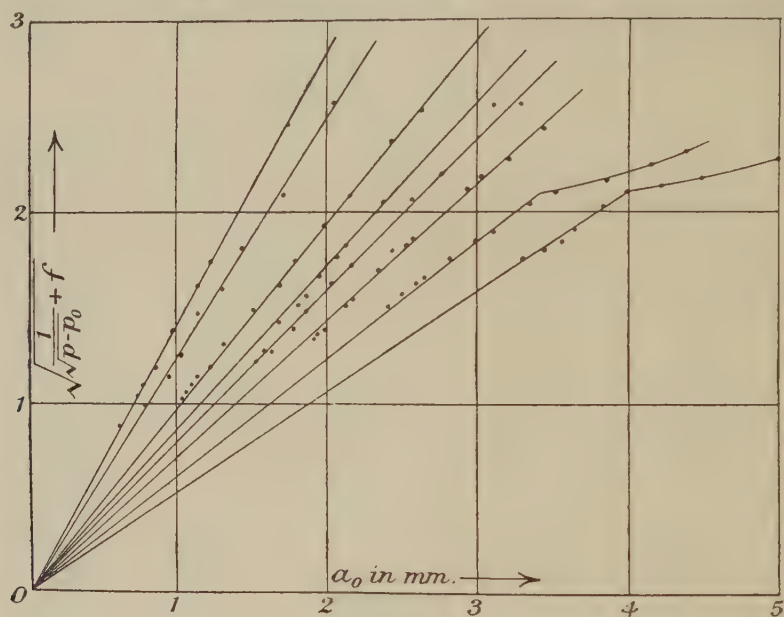


FIG. 6.

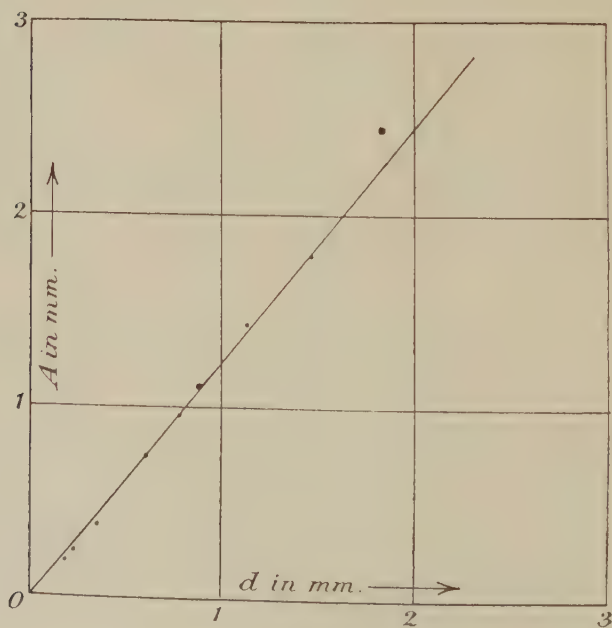


FIG. 7.



the origin (Fig. 7). (The only exception is shown by a value of  $A$  found for a very wide slit,  $d=0.188$  cm.)

From this graph we have

$$A=1.22(5)d.$$

The equation is now

$$\frac{1}{v}=\lambda(a_0^2-A^2)=\lambda(a_0^2-1.50d^2)$$

the gradient  $\lambda$  is of the dimensions  $\left(\frac{T}{L^3}\right)$ . Since  $\lambda$  can only depend on the slit-

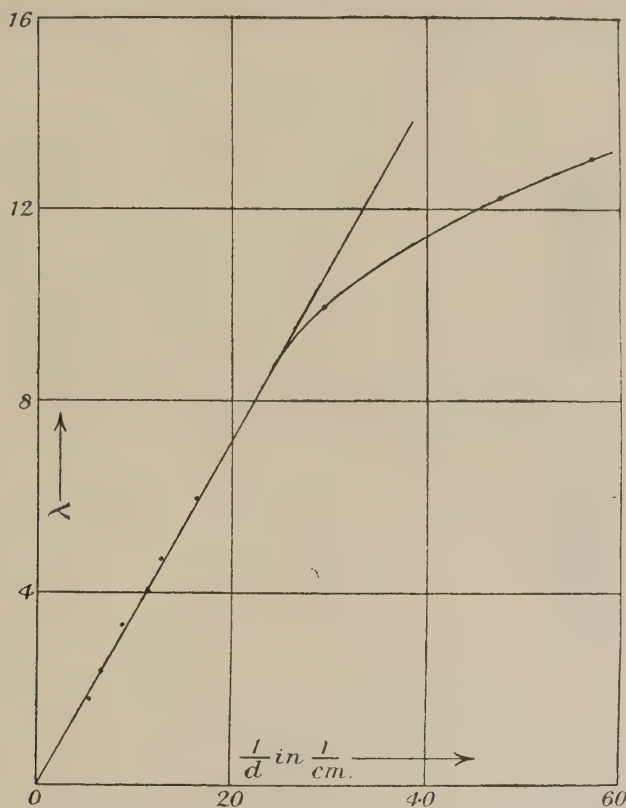


FIG. 8.

width  $d$ , and on the nature of the gas used, one might assume that its dimensions are  $\left(\frac{T}{L^3} \cdot \frac{1}{L}\right)$ , in which the length is the width of the slit.

Fig. 8 shows the effect of plotting  $\frac{1}{v}$  against  $\lambda$ . For all slit-widths greater than

0.035 cm. the relation is that of a straight line passing through the origin. If  $B$  be a numerical constant, we have

$$B \frac{\eta}{\rho} \cdot \frac{d}{v} = a_0^2 - 1.50d^2$$

or

$$B \left( \frac{v}{vd} \right) = \left( \frac{a_0}{d} \right)^2 - 1.50$$

which embodies the principle of dynamic similarity.

#### F. THE TONAL BOUNDARY.

The occurrence of the distance  $a_0$  is due to the departure of the tonal boundary from the straight lines. If the edge is at a distance  $a$  from the slit, an eddy-centre is formed near the slit at a distance

$$\frac{v}{2} = \frac{h}{l} \cdot \frac{a}{2}$$

from the principal plane (Fig. 9). From the boundary maps it appears that normal

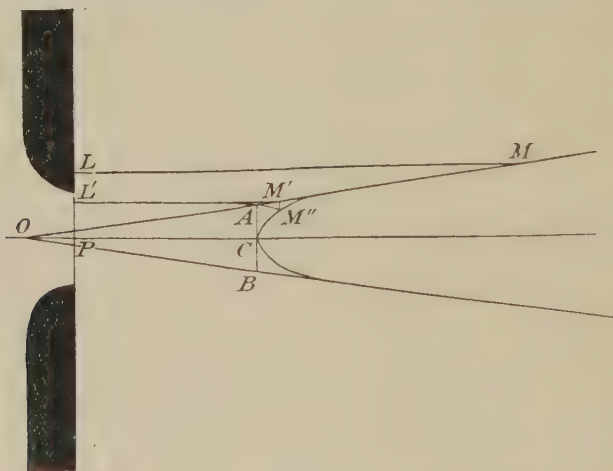


FIG. 9.

an eddy formed at a position  $L$  moves along the straight line  $LM$ , and can be intercepted by the edge at  $M$ . An eddy formed at  $L'$ , however, can be intercepted by the edge at  $M''$ , having moved inwards a distance  $M'M''$  in traversing the distance parallel to  $PX$ . The normal case may correspond to an eddy moving as a roll between air at high and air at low velocity. The abnormal case may be due to the movement of an eddy in a field of forward moving air having a steep velocity gradient at right angles to the direction of motion. To obtain an expression for the force on a unit length of a rectilinear vortex of strength  $M$  moving in a field of uniform velocity relative to the eddy centre, Prandtl used the equation

$$\begin{aligned} & \text{(Rate of change of upward vertical momentum)} \\ & = \text{(resultant upward pressure on surface of bounding cylinder)} \\ & + \text{(resultant upward vertical pressure due to the body—in this case, fluid within the cylinder),} \end{aligned}$$

and hence found that the force per unit length in a direction at right angles to the velocity of the field is  $V\rho M$ . Using this equation, I find that in a field of uniform velocity-gradient, the acceleration of the eddy at right angles to the velocity field is, as a first approximation, of the form  $\left(c_1MV + c_2MV\frac{\partial V}{\partial y}\right)$ , where  $V$  is the velocity of the field relative to the eddy-centre. About a laminar jet  $\frac{\partial V}{\partial y}$  is very great, so that it is possible that only the second term is of importance. The frequency observations (to be published later) show that one can assume  $\frac{\partial V}{\partial a} = 0$ . Since  $M$ , the eddy-strength, must, in the case of edge-tones, also depend on the total quantity of air leaving the jet per second, we may assume the motion of the eddy to be given by

$$\frac{\partial a}{\partial t} = \text{const.} = \alpha V_0$$

$$\frac{\partial^2 y}{\partial t^2} = KV_0(V - \alpha V_0) \frac{\partial V}{\partial y}$$

where  $V_0$  is the velocity of the fluid in the principal plane (i.e., the maximum velocity of the jet), and the product  $KV_0$  has no dimensions

then 
$$t=0, y=y_0; \quad \frac{\partial y}{\partial t} = 0; \quad \frac{\partial a}{\partial t} = \alpha V_0; \quad a=0.$$

Assume the distribution of velocity about the principal plane to be of the form

$$V = V_0 e^{-ny}$$

where  $1/n$  is a length, probably the slit-width.

Then, by two integrations and substitution,

$$\frac{e^{ny}}{e^{ny_0}} = \cos \left( \frac{n}{\alpha^2} \cdot e^{-ny_0} \sqrt{KV_0} \cdot a \right)$$

one might assume  $K = \frac{cd}{v}$ , where  $c$  is a numerical constant.

then when

$$y=0, \quad a=a_0$$

$$c \cdot \frac{d \cdot V_0}{v} \cdot a_0^2 = \text{a constant (depending on } n, \alpha \text{ and } y_0)$$

which is somewhat similar to the experimental result.

It was therefore desirable to know the exact form of the nose of the tonal boundaries. The distances involved are very small, and the curve approaches the axis  $y=0$  very steeply. One source of error, a possible slight transverse movement of the apparatus relative to the edge, was eliminated by plotting the total possible transverse movement  $y$  against  $a$ .

Fig. 10 shows some of the curves obtained in this way, drawn to a very large



scale. The following formula was found to satisfy the shape of the curves for wide slits:—

$$y = \frac{h_-}{l} a - \frac{h_-}{l} a_0 \cdot e^{-(m^2 \bar{a}^2 - m^2 \bar{a}_0^2)}$$

or

$$ye^{m^2 \bar{a}^2} = \frac{h_-}{l} \left( \bar{a} e^{m^2 \bar{a}^2} - \bar{a}_0 e^{m^2 \bar{a}_0^2} \right)$$

in which  $a_0$  and  $\bar{a}$  denote  $a_0$  and  $a$  respectively, plus the distances from the pole to the origin 0.

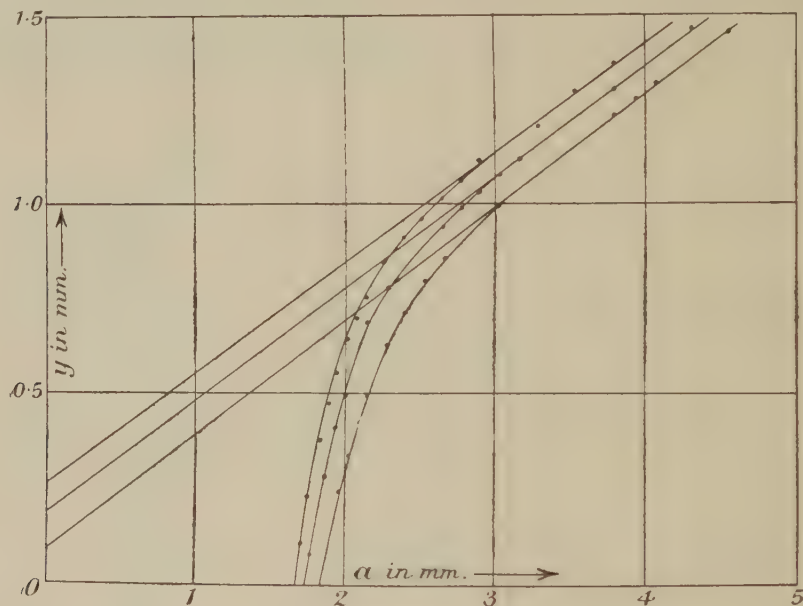


FIG. 10.

$a_0$  and  $a$  were measured from  $P$ .  $\bar{a}_0$  and  $\bar{a}$  are measured from 0.

By plotting  $\log_e \left( \frac{\frac{h_-}{l} a_0}{\frac{h_-}{l} a - y} \right)$  against  $(\bar{a}^2 - \bar{a}_0^2)$

(Fig. 11), it is seen that diagrams made with the same slit-width but different pressures yield the same value of  $m$ . Moreover,  $1/m$  must be dimensionally a length. For very wide slits  $1/m$  was found to be very nearly equal to the slit-width. For less broad slits,  $1/m$  is always greater than  $d$ . For narrow slits this only holds over small range of  $(\bar{a}^2 - \bar{a}_0^2)$ , after which there occurs a sudden change of gradient (Fig. 12).

G. CONCLUSION.

In the above work a narrow slit has always implied a slit of width less than 0.35 cm. It is strange that this width appears to be absolute for air. Kohlrausch

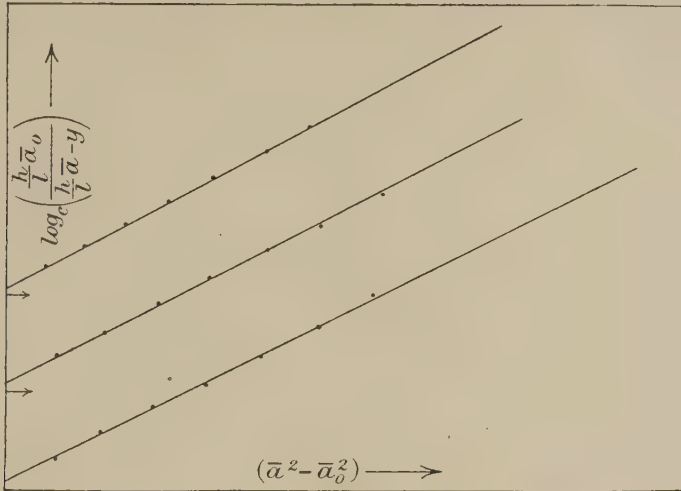


FIG. 11.

and the same value in his work on slit-tones, exhibiting a demarcation between broad and narrow slits.

The boundary maps, moreover, give further support to the above suggestion

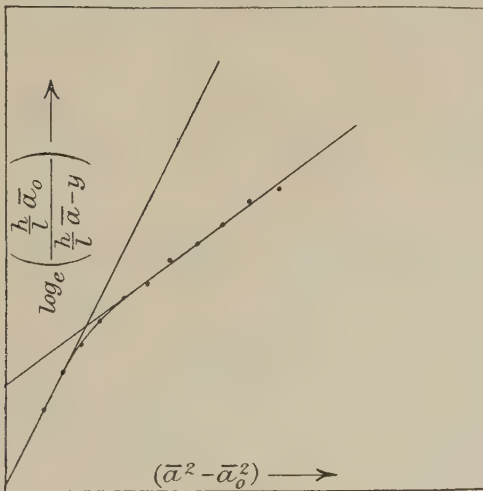


FIG. 12.

the deflection of an eddy in a steep velocity gradient. We know that when the pressure is increased the whole map advances towards the slit. Since, however, the

slope  $\frac{h}{l}$  changes slightly with the pressure, the distance  $OC$  (Fig. 9) is not a constant for the slit-width. The maps, however, show that for wide slits the distance  $AB$  (the separation of the straight-line boundaries at the nose) is apparently constant. In Table II are given the values of the ratio  $AB/d$  for various slit-widths. This

TABLE II.

$d$	Pressure in cm. of water	$\frac{AB}{d}$
0.077 cm.	0.34	0.64
	0.62	0.69
0.104 cm.	0.38	0.68
	0.63	0.65
0.133 cm.	0.25	0.68
	0.45	0.68
0.181 cm.	0.14	0.65
	0.29	0.67

means that when the edge is at the distance  $a=a_0$  from a wide slit the eddies are being produced at distances about  $\frac{0.67}{2}d$  on either side of the principal plane, and are being deflected by that entire amount in their passage to the edge. Such eddies, therefore, originate *in the mouth of the slit*, in a field of high velocity-gradient. With narrow slits this field will be less broad, and the range of  $(\tilde{a}^2 - \tilde{a}_0^2)$  over which one may hope to find a uniform law of deflection, proportionally smaller. As  $a$  is increased, the eddies will originate further from the principal plane, until they move on lines remote from the influence of the slit and are undeflected in their uniform progress.

In conclusion, I would like to express my gratitude to Prof. S. W. J. Smith for granting me such excellent facilities for the execution of these experiments, and for his encouragement during the course of the work.

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## DISCUSSION.

Sir RICHARD PAGET said that the author's work might be of great value in connexion with the design of organ pipes. It is a curious fact that if the walls of the channel leading to the jet-orifice are smooth the tone obtained is not so good as that given by rippled walls.

Dr. W. S. TUCKER complimented the author on his painstaking work, which has opened the way for further research. As a source of sound for experimental purposes the organ pipe has proved very unsatisfactory, as its behaviour is to a great extent incalculable. The jet as a source of sound is coupled with the pipe as a resonator, and the reaction between the two presents a complicated problem; and then any variation in the velocity of the jet will affect the rate of production of eddies. The quality and intensity of the resulting tone depends on all these factors, and the present Paper should point the way to a better understanding of the mechanism of the process.

Dr. G. W. C. KAYE said that at the National Physical Laboratory the organ pipe has had to be abandoned as a source of sound. Possibly the author might be able to improve the design of such pipes so as to render them suitable for laboratory use.

Mr. E. G. RICHARDSON said that about a year ago he read a Paper to the Society on a somewhat similar subject; he had employed the method of Kruger, who, however, had been unable to get results. The Paper in question was devoted to a study of æolian tones, and an annular jet was employed, as opposed to the author's ribbon-shaped jet; but curves similar to those of the author's Fig. 4 were obtained for jets of smoke and water. The author's measurements are some of the most careful that have been made, and he has followed a new line of inquiry, as previous experiments have dealt mainly with the question of frequency. His plan of measuring the depth of the jet is a very sound one. Although Kármán first applied the eddy theory to experimental work, credit must also be given to Bénard, who put it forward seven or eight years earlier. As regards the streamlining of the author's orifices, this plan would affect the value of  $a_0$ , in consonance with results obtained by the speaker and Mr. Tyler. There is rather a puzzling connexion between the frequency and the distance of the edge from the orifice; the distance between the eddies appears to adapt itself to this distance. No very satisfactory explanation of this phenomenon has been offered.

Mr. E. TYLER (communicated): With reference to this very interesting Paper I should like to congratulate the author on his very careful work in dealing with such a difficult problem, and I should furthermore like to point out that in his determination of small tonal boundary measurements he claims to measure these to .00025 cms., whereas the accuracy of movement of the wedge is about .001 cm. On what assumptions does the author claim such accuracy of small measurements? Has the author tested microscopically for any vibration of the support that might occur during the production of the edge-tones, for with such a wedge as used by the author there is a possibility of Æolian Tone phenomena.

The results shown in Fig. 4 are very interesting indeed and resemble similar characteristic liquid jet curves published by Dr. Richardson and myself (Proc. Physical Society, August, 1925). I rather regret the author has plotted values of  $a_0$  (minimum) against the pressure (cms. of water), for a better comparison no doubt could be made by plotting  $a_0$  against  $v$ . (vel. of air stream). As the author considered whether viscosity is a factor modifying the shape of these curves, and if so, what are his views?

Referring to Fig. 5, I do not see any justification in continuing the curves back in such a manner so as to cut the  $\frac{1}{\sqrt{p-p_0}}$  axis below 0 at points where  $a_0=0$  giving a value for  $\frac{1}{\sqrt{p-p_0}}=-f$ .

Unless to satisfy the condition shown in Fig. 6, i.e., the  $\sqrt{\frac{1}{\sqrt{p-p_0}}}+f$ ,  $a_0$  curves all intersect at the origin. There is no reason why the curves in Fig. 5 could not be all continued to at one point below 0 at a constant  $f$ . This result would thus modify the curves in Fig. 6.

AUTHOR'S reply: I am very grateful for these comments and criticism on my Paper. S. Richard Paget has mentioned the design of the throat of an organ-pipe. I am aware of the practice of "nicking" the slit, but organ-builders only perform this operation on pipes of certain stops, to which it is supposed to impart rapidity and brightness of speech. The practice must have an important bearing on the production of edge-tones, but at present I have made no experiments in this direction.

Dr. Tucker and Dr. Kaye have spoken of the unreliability of the organ-pipe as a standard source of sound. This is not unavoidable, but I can see no prospect of a pipe ever being made which will compare favourably with a standard fork. The degree of coupling between a pipe and the edge-tones formed at its mouth has been examined very ably by Prof. Camière at Toulouse (Journ. Phys. et Rad., Février, 1925).

I am glad that Dr. Richardson has raised the question of Bénard's work in relation to vortex-systems. In calling the arrangement a Kármán system I am only following Prandtl's school who quite rightly give Kármán the credit of having established the theory of this system without wishing in the least to depreciate the value of Bénard's experiments and observations. By streamlining the slit a jet was obtained of an ideally simple type, and any change in the value of  $a_0$  obtained by this method must be a change for greater simplicity. The question of frequency will be dealt with in the second Paper.

In thanking Mr. Tyler for his communication I regret that my brief statement of the accuracy of movement of the edge should lead to misunderstanding. The total error of the screws over so great a distance as 1 cm. may be as great as .001 cm., but over the minute distances measured in the tonal boundaries, the error did not exceed .00025 cm. My assumption of such accuracy is based on comparative measurements at different positions on the screws over two thousand observations having been made in the measurements of these tonal boundaries alone.

Mr. Tyler is mistaken in believing that Æolian phenomena may ever arise behind the forward edge of a surface parallel to the direction of flow. A necessary condition for Æolian tones is freedom for the eddies formed on one side of the obstacle to move under the influence of the eddies liberated on the other side. With a wall boundary that is impossible. There is a very simple and absolutely sure method of testing for vibration in the edge. On placing the fingers on the side of the edge no change in the pitch or quality of the tone occurs. Nor are the values of  $a_0$  and  $\gamma$  affected. It is recognized that a light touch by the fingers will immediately damp out all vibrations except those of very high frequency in great thickness of metal.

Mr. Tyler will find the answers to his questions concerning velocity and viscosity in the Paper itself. I fail to understand his suggestion that a given family of experimental curves may be produced at will to pass through a given point, since if a curve is to retain the character given by experiment it may only be produced in one way. This has been done in Fig. 5. No was it necessary to obtain the values of " $f$ " for the determination of the equation of dynamic similarity, as the values of  $A$  yield the same result. I trust that a second Paper will bring out the relative importance of the different factors with more clearness than has been possible in this first communication.

V.—THE SPECTROSCOPIC DETECTION OF MINUTE QUANTITIES OF MERCURY.

By J. J. MANLEY, M.A., Research Fellow, Magdalen College, Oxford.

*Received October 18, 1925.*

ABSTRACT.

Details are given of a method whereby vertical spectrum tubes (demanded by certain investigations) can be critically examined for vanishingly small quantities of mercury. The tubes are two U-tubes partially immersed in insulated water. The water serves as external electrodes. End-on view of the glow within the excited tube is obtained by a totally reflecting prism placed upon the summit of one of the limbs. The light is thus deflected horizontally and received the usual way by a spectrometer.

RECENTLY I have found it necessary to examine spectroscopically the low pressure and gaseous contents of some U-tubes for minute quantities of mercury.

The U-tubes, having a length of 24 cms. and an internal diameter of 1.2 mm. less, formed parts of some permanent apparatus; and, owing to the conditions required for experimenting, the tubes were of necessity situated vertically. Under these circumstances, the only view obtainable with a Hilger wavelength spectrometer was one at right angles to the axis of the tube, and this was not always sufficiently sensitive. A further difficulty arose from the fact that internal electrodes for producing a discharge were not permissible. The weight of the mercury that might be present varied from a maximum of 0.0002 grm. to a quantity vanishingly small. Initially, the plan adopted was that indicated in Fig. 1.

$A$  and  $B_1$  represent two U-tubes, each having the dimensions noted above. The mercury was sought for in the tube  $B_1$ . External electrodes were provided by the partial immersion of the tubes in water contained in the insulated beakers  $C$ ,  $D$ . Wires from the high potential terminals of the induction coil  $I$  were led into the contents of  $C$  and  $D$ . When the coil was activated with a 6-volt accumulator  $G$ , the limbs  $j$ ,  $k$  were filled, like an ordinary spectrum tube, with a bright glow; hence a section of  $k$  could be examined with the spectrometer. This simple device proved amply sufficient for all those cases in which the mercury present in  $k$  attained or exceeded some as yet undetermined limit; the plan, however, failed when the amount of the element in the tube was infinitesimal. For aiding in the detection of vanishingly small quantities, the modified U-tube  $B_2$  shown in Fig. 2 was designed. It was constructed as follows:

First a T-piece was made, and one of its three limbs shortened to 3 mm. The short limb was then closed by a glass rod which was fused to it. During the fusion work was so conducted that the attached end of the rod presented a flat surface  $\frac{1}{16}$  in. Next, the rod was melted and rotated in a blowpipe flame until it had assumed a form almost truly spherical.\* After annealing, two plane faces were by

\* A suitable sphere is one having a radius of 5 mm. The length of glass rod required for its construction is calculated at the outset. The complete sphere is indicated by the dotted line.



means of carborundum powder and turpentine, ground upon the sphere ; one of the faces ( $\alpha$ ) was vertical, the other ( $\beta$ ) intersected  $\alpha$  as shown, at an angle of  $45^\circ$ . Each face was then smeared with Canada balsam and covered with a thin glass plate. The required plates were cut from a cover slip used for work with the microscope. Made thus, the totally reflecting glass prism  $P$  was extremely satisfactory. Finally

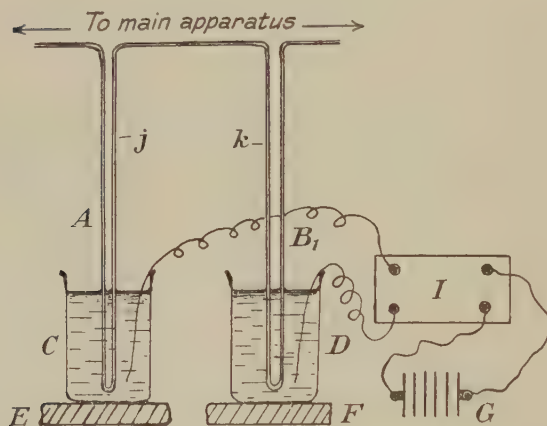


FIG. 1.

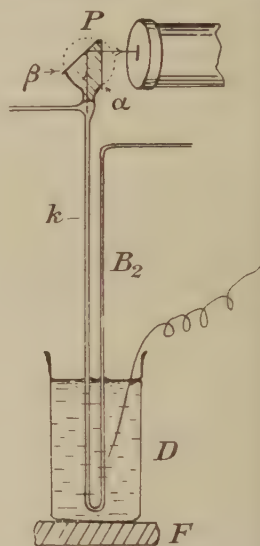


FIG. 2.

the long limb  $k$  of the T-piece was bent U-wise, as seen in Fig. 2, and the whole substituted for the simpler tube  $B_1$  of Fig. 1. By placing the spectrometer slit near the face  $\alpha$  and activating the coil, an end-on view of the glow in  $k$  is obtained by reflection, and spectral lines otherwise invisible or but feebly seen are revealed more or less prominently.

# XVI.—ON THE STORAGE OF SMALL QUANTITIES OF GAS AT LOW PRESSURES.

By J. J. MANLEY, M.A., Research Fellow, Magdalen College, Oxford.

Received November 11, 1925.

## ABSTRACT.

The author describes and gives a figure of an apparatus used for storing small quantities of pure or highly purified gases in such a way that contaminating air is excluded. The apparatus is designed for use in conjunction with a Sprengel pump, which withdraws the gas from any experimental plant and delivers it into the storage apparatus. With the aid of barometric traps, etc., the gas can be readmitted either partially or wholly into the experimental plant.

DURING a research conducted with pure helium at pressures varying from 1-12 mm. of mercury, it has frequently been necessary to modify the experimental apparatus. At the outset the helium was on each occasion first withdrawn by a Sprengel pump and collected in a tube; subsequently it was returned to the apparatus by means of a specially constructed pipette. In every instance after the re-introduction of the helium a spectral analysis revealed the presence of decided traces of air. If the apparatus had been small and compact, the impurity could have been quickly removed by circulating the gases over charcoal cooled by liquid air; but in the present case the primary portions of the apparatus were connected by tubes having capillary dimensions and great length, also the total volume of the apparatus was considerable; hence much time was required for completing the absorption of the contaminating gas. Ultimately this difficulty was avoided by the use of the storage apparatus depicted in Fig. 1. From the figure it may be seen that the apparatus communicates (a) with the main or experimental apparatus through the tube *m*, to which it is fused, and (b) with a twinned barometric column *R*, and that the whole in conjunction with the main apparatus can be evacuated by a Sprengel pump *P*.

The highly purified helium was at the first introduced by way of the limb  $\beta$ , the mercury trap *J* being open; a similar trap *K* was either open or closed as circumstances demanded (*vide infra*). For effecting alterations in the form of the experimental apparatus the procedure is as follows.

First the trap *J* is closed by raising the cistern *E*, so that the mercury attains some such level as *a* . . . *b*; the tap *t*<sub>1</sub> is then shut. Next, the open end of the limb  $\beta$  is placed over the jet of the fall-tube of the Sprengel pump as shown. This operation is rendered possible and perfectly safe by the flexibility of the upper connecting tubes, which are long and narrow. The pump is now brought into action, and the gas thus transferred from the experimental to the storage apparatus. The helium having been removed, the limb  $\beta$  is withdrawn from the jet and the main apparatus filled with dry and carbon dioxide-free air. With the entry of the air, the mercury in the trap *J* rises to something less than barometric height in the tube

above *b*. The desired alterations in the main apparatus may now be undertaken and when completed the whole apparatus is again highly evacuated. On lowering

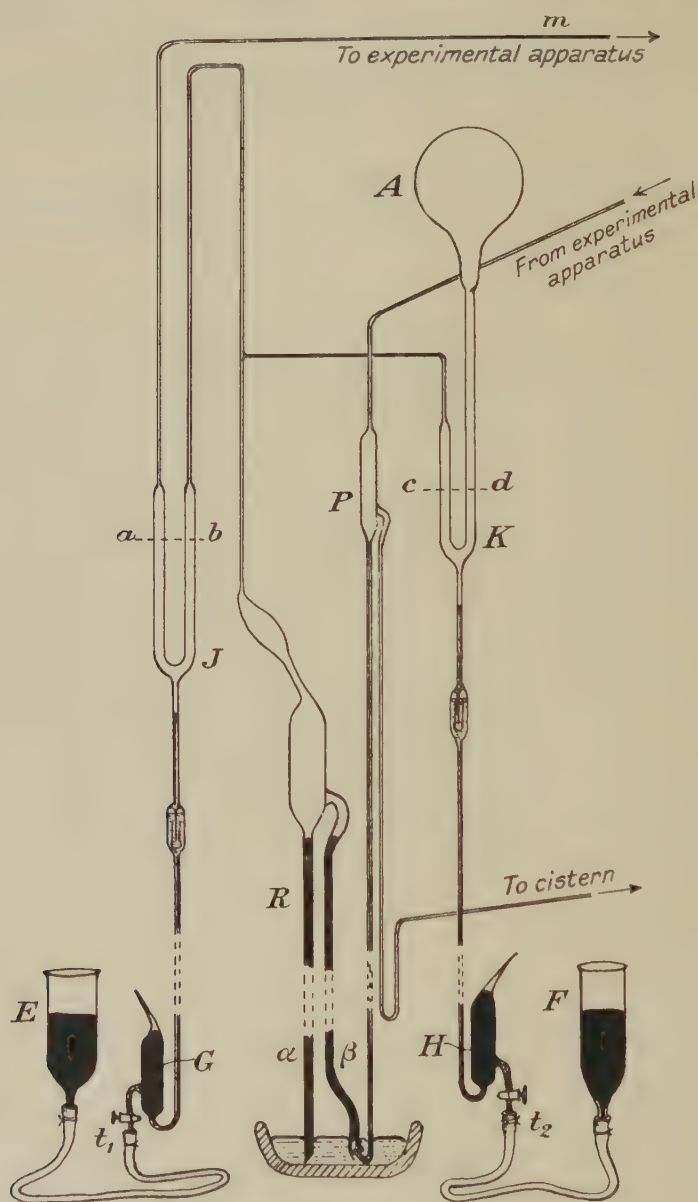


FIG. 1.

the cistern *E* and opening the tap  $t_1$ , the trap *J* is freed from mercury and the stored gas flows back into the apparatus for further experiments.



It may be noted that the effective volume of the storage apparatus depicted in Fig. 1 can be varied. If the volume of the gas to be stored is relatively small, the bulb *A* is not required. In that case *A* is trapped off by raising the cistern *F* so that the mercury stands at the level *c . . . d*, and the tap *t*<sub>2</sub> closed. Again, if for new experiments to be carried out after the storage and subsequent release of the gas, a portion only of the helium is required, the trap *K* is kept open whilst the gas is being stored, and then closed before *J* is opened. If necessary, the quantity of the gas in the experimental apparatus can at any moment be increased by suitably manipulating the cistern *F*.

## XVII.—THE EFFECT OF ROLLING ON THE CRYSTAL STRUCTURE OF ALUMINIUM.

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### ABSTRACT.

Sheets of aluminium have been examined by the ionisation spectrometer and by photographic methods, with a view to discriminating between two contradictory results obtained by previous observers with the photographic method as to the final orientation of crystals in rolled material.

The results show that, when a cast specimen of aluminium containing a number of large crystals oriented at random throughout the body of the material is rolled, the crystals break up into a large number of minute crystals. As the thickness of the material is progressively diminished, the small crystals tend to take up a definite orientation, each crystal having a cube diagonal in the direction of rolling and a (211) plane in the plane of rolling. Two sets of crystals exist in the material after rolling, the one set being the optical image of the other in the plane of rolling.

The observations obtained by the ionisation spectrometer indicate that the type of the space lattice remains unaltered, and that the parameter of the material in the severely worked condition does not differ from that of the annealed material by more than 0.5 per cent.

### INTRODUCTORY.

THE orientation of the crystals in rolled aluminium sheets of thickness 0.015 mm. has been examined by Mark and Weissenberg,\* who concluded that in the rolled condition the crystals were oriented with a (110) plane parallel to the plane of rolling with a divergence of  $\pm 35^\circ$  and a (112) direction parallel to the direction of the rolling with a divergence of  $\pm 8^\circ$ . This arrangement places the cube diagonal (111) in the surface of the foil perpendicular to the direction of rolling, as in Fig. 1a. Further work on the same subject by Wever† led him to the conclusion that a (111) direction lay parallel to the direction of rolling, a (110) parallel to the transverse direction, and a (112) parallel to the foil normal, as in Fig. 1b. These discordant results were obtained by photographic methods.

The experiments, a description of which follows, are now published with a view to discriminating between the above conclusions. Sheets of aluminium have been examined by the ionisation spectrometer and by the photographic method, the former having the advantage that direct measurements can be made of the angle between planes in the same zone.

### I. EXPERIMENTS WITH THE IONISATION SPECTROMETER.

#### *Examination of Cast Specimen of Aluminium.*

The crystal grains in the etched surface of the specimen of cast aluminium (1.06 cm. thick, 2 cms. wide and 6 cms. long) employed, were about 1 to 2 mm. across. The specimen was mounted on the spectrometer table with its length parallel to the

\* Zeitschrift für Physik., 14, p. 328 (1923), and 16, p. 314 (1923).

† Zeitschrift für Physik., 28, p. 69 (1924).

axis of the instrument, and its surface parallel to the incident beam of X-rays from the molybdenum anticathode. The widths of the bulb, crystal and chamber slits were 1 mm., 4 mm. and 0.5 mm. respectively. The chamber was set at the appropriate angle to receive reflections from the (111) planes. The crystal table was rotated, and readings of the intensity were taken at intervals of  $\frac{1}{4}^\circ$ . This procedure was repeated with the ionisation chamber set to receive the reflections from the

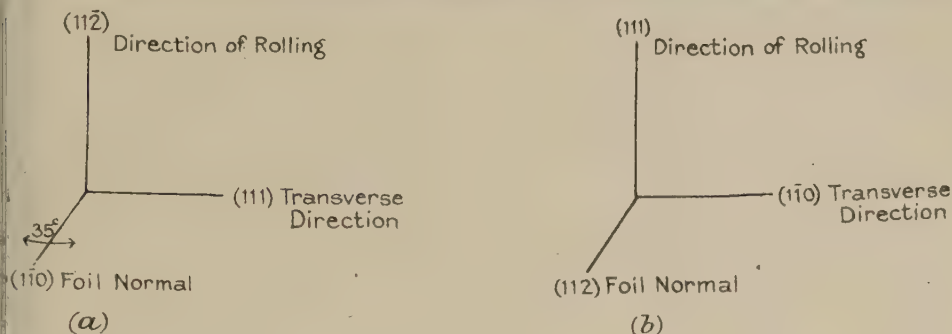


FIG. 1.

(100), (110) and (311) planes. The results are shown in Fig. 2, the peaks representing the effect of the single crystals as they are brought successively into the reflecting position by the rotation of the specimen.

#### Examination of Rolled Specimen after a 14.2 per cent. Reduction in Thickness.

The specimen was now marked by means of saw cuts on the edges, so that after rolling the same region could be again examined. The thickness was reduced from

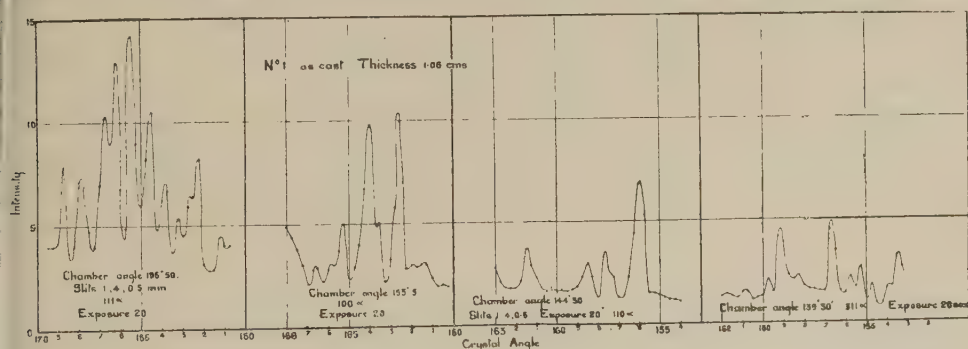


FIG. 2.

1.06 cm. to 0.91 cm., and the above observations repeated with the direction of rolling parallel to the spectrometer axis and the chamber set to receive the rays reflected from the (111), (100) and (110) planes as before. The results are shown in Fig. 3a, and it will be seen that the intensity curves no longer show a series of sharp maxima and minima, but are approximately smooth, showing that the large crystals



originally present have been broken up into a large number of minute crystals. The surface of the specimen was now deeply etched, and the observations repeated with a view to ascertaining whether the effect was present throughout the mass of the material or whether it was localised on the surface. It was found that etching did not alter the nature of the curves already obtained, so that the breaking up of the large crystals takes place, if not right through the material, at any rate to very considerable depth—of the order of at least a few millimetres.

*Examination of Rolled Specimen after Successive Reductions in Thickness ranging from 57.5 per cent. to 99.0 per cent.*

The rolling was proceeded with, and similar observations taken at thicknesses of 0.45 cm., 0.23 cm. and 0.01 cm. The intensity of the reflections diminished as

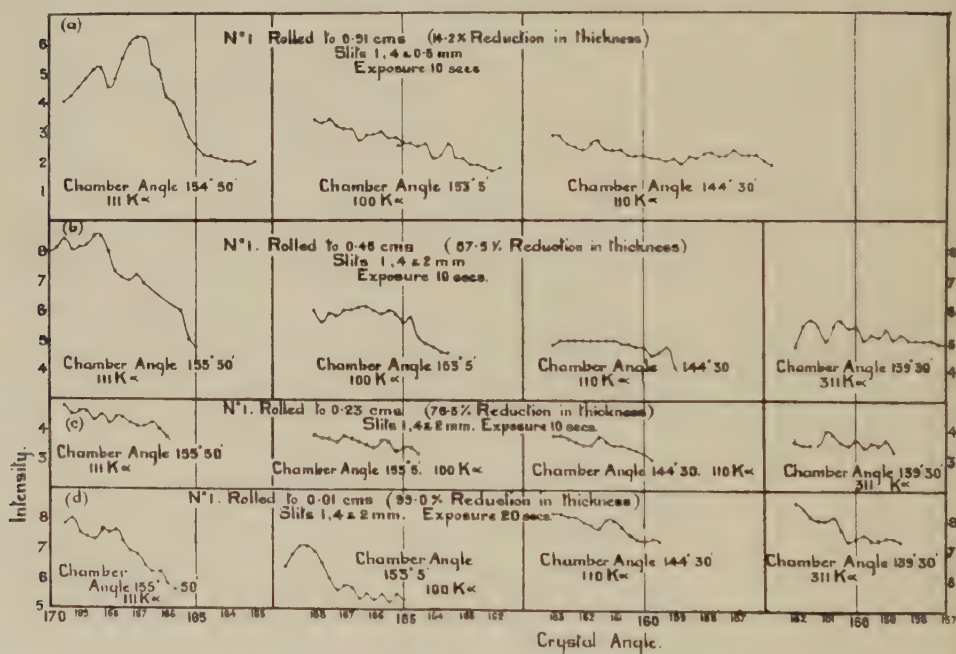


FIG. 3.

the thickness of the specimen decreased, so that the chamber slit had to be opened to 2 mm. for this series of observations. The only new fact observable from these curves is that the intensity of the (110) and (311) reflections becomes gradually greater, and finally exceeds the intensities of the (111) and (100) reflections, as shown in Fig. 3 (b, c and d). The same fact is also illustrated in Fig. 4, which shows parts of the spectrum obtained from the surface of the metal when reduced to the thicknesses above mentioned, the chamber in this case being rotated at twice the rate of the crystal. The relative diminution of intensity of the (100) reflections is particularly marked. In the specimen of thickness 0.01 cm. (Fig. 4c), the (111) reflec-

tions are comparatively feeble and displaced, (100) is hardly discernable, while (110) and (311) are both intense. In all specimens of this thickness which we have examined the (100) reflections from the surface are absent. The (111) reflections are always displaced about  $\frac{1}{2}^\circ$  towards the origin, and (110) and (311) reflections are particularly intense and in their correct positions. The value of the parameter,

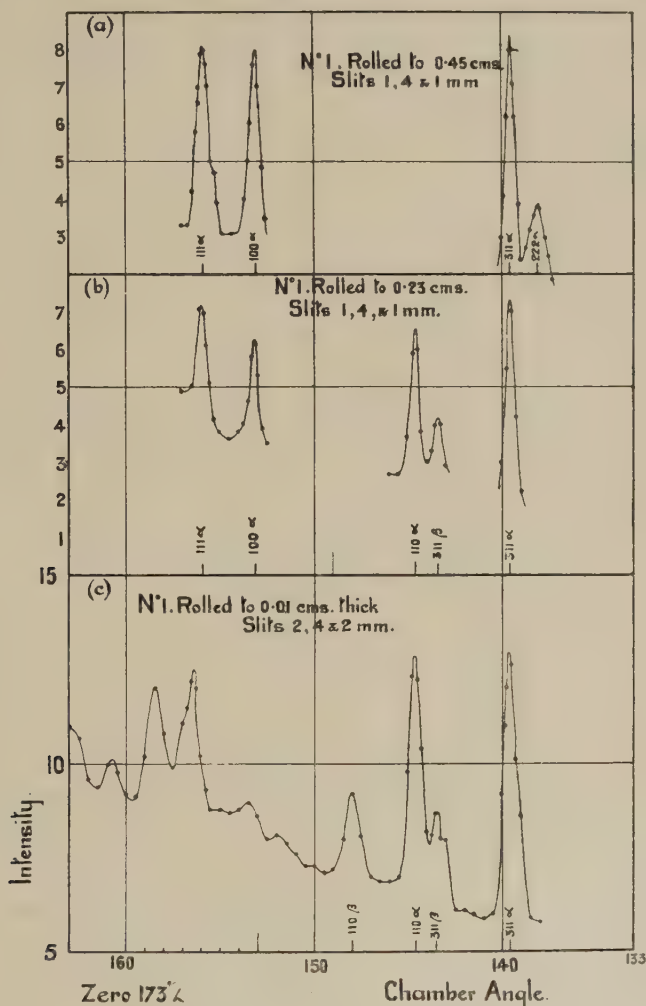


FIG. 4.

as determined from the observed reflections, does not differ from that of aluminium in the unworked state. The results obtained from the observations of Fig. 4 are given in Tables I, II and III, and show that the parameter of the lattice has remained unaltered.

TABLE I.  
Thickness = 0.45 cm. (Fig. 4a).  $K\alpha = 0.7078\text{\AA}$ .  
 $K\beta = 0.630\text{\AA}$ .

Reading of intensity maximum.	Glancing angle $\theta$	Form.	$\lambda$	Sin $\theta$	$a$
155°53'	8°43'	111	$K\alpha$	0.1515	4.046 $\text{\AA}$ .
153 6	10 6	200	$K\alpha$	0.1754	4.036
139 33	16 53	311	$K\alpha$	0.2904	4.042
138 6	17 36	222	$K\alpha$	0.3024	4.053
					Mean $a = 4.044\text{\AA}$ .

TABLE II.  
Thickness = 0.23 cm. (Fig. 4b).

Reading of intensity maximum.	$\theta$	Form.	$\lambda$	Sin $\theta$	$a$
155°57'	8°40'	111	$K\alpha$	0.1507	4.067 $\text{\AA}$ .
153 9	10 4	200	$K\alpha$	0.1748	4.049
144 38	14 20	220	$K\alpha$	0.2476	4.043
143 23	14 58	311	$K\beta$	0.2582	4.047
139 34	16 52	311	$K\alpha$	0.2901	4.046
					Mean $a = 4.050\text{\AA}$ .

TABLE III.  
Thickness = 0.01 cm. (Fig. 4c).

Reading of intensity maximum.	$\theta$	Form.	$\lambda$	$a$
144°37'	14°20'	220	$K\alpha$	4.042 $\text{\AA}$ .
139 36	16 51	311	$K\alpha$	4.049
				Mean $a = 4.045$ .

The results agree with each other to 0.25 per cent., which is within the limits of accuracy of the observations.

The peculiarities of the spectrum shown in Fig. 4c are typical of the material when reduced to a thickness of 0.01 cm., and are not to be ascribed to any change in the type or in the dimensions of the space lattice. They can be explained by supposing that the crystals of which the metal is composed are all orientated in a particular direction.

In the experiments just described the direction of rolling was vertical, i.e., parallel to the axis of the spectrometer.

*Examination of specimen with direction of rolling horizontal.*

Five of the sheets of thickness 0.01 cm. were laid flat on one another and mounted on the spectrometer table with the direction of rolling of each sheet lying in a horizontal plane. The chamber of the spectrometer was set to receive reflections from the (111) planes and the specimen rotated. A maximum of intensity was



found with the specimen nearly perpendicular to the incident beam, and the best position of the chamber was found to be at  $157.25^\circ$  ( $16^\circ 3'$  from the direct beam). The peaks obtained with this chamber setting are shown in Fig. 5*b*. The shift of the (111) peak from  $17^\circ 23'$  to  $16^\circ 3'$  can in this case be accounted for by the divergence of the primary and reflected beams, the bulb and crystal slits being at 2 mm. and 4 mm. respectively and separated by 7 cms. When these slits were cut down to 1 mm. each, the displacement of the peak was reduced to  $12'$ .

The width of the middle peak is about  $40^\circ$ , a few degrees of which are accounted

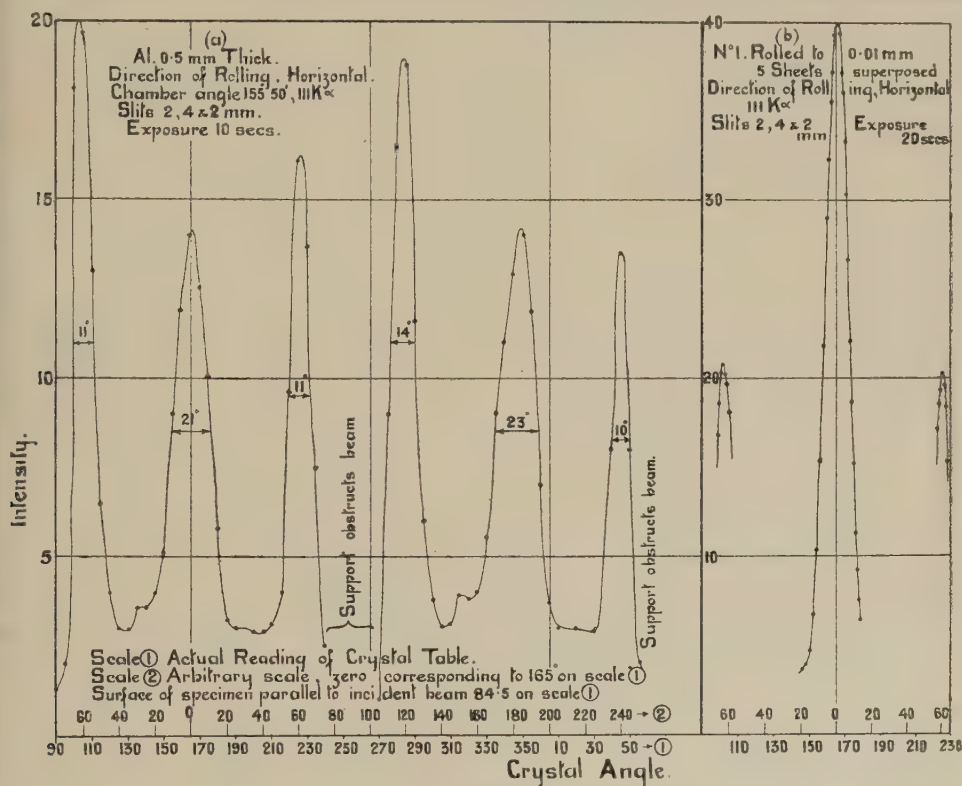


FIG. 5.

for by the angular width of the incident beam. Part of the width of the peak might also be due to the sheets of which the specimen was composed not being parallel to one another. As it was impossible to fix the thin sheets together so that they were rigorously parallel, it was decided to continue the work with fresh material rolled from 1 cm. to 0.05 cm. in thickness.

*Experiments with rolled aluminium sheet 0.05 cm. thick. Direction of rolling horizontal.*

(A) *Rotation of specimen about a vertical axis.*—A sheet of aluminium was rolled down to a thickness of 0.05 cm., being passed through the rolls always in the same direction. A plate of the material was mounted on the spectrometer with its surface in a vertical plane and with the direction of rolling horizontal as before, the chamber

set at the proper angle ( $155^{\circ}50'$ ) to receive the (111) reflections and the specimen rotated, readings being taken every  $5^{\circ}$ . The observations were repeated with the ionization chamber set to receive the (100) and (110) reflections. The results of the three series are shown in Figs. 5*a*, 6*a* and 6*b*.

The second peak from the left of Fig. 5*a* occurs at an angle of  $166^{\circ}$  on the scale of the crystal table. The angle of reflections from the (111) planes of aluminium is  $8.7^{\circ}$ , so the planes giving this peak are on the average parallel to the incident beam when the reading of the crystal scale is  $174.7^{\circ}$ . The surface of the sheet is

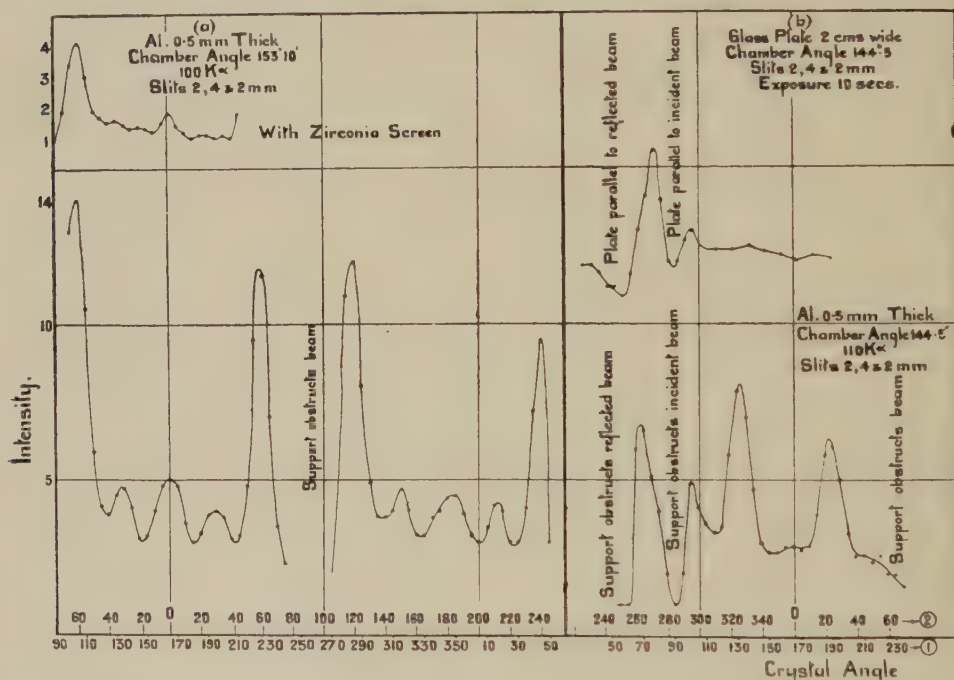


FIG. 6.

parallel to the incident beam at a scale reading of  $84.5^{\circ}$ , so that at a scale reading of  $174.7^{\circ}$  the surface is inclined at  $90.2^{\circ}$  to the beam. This set of (111) planes is accordingly at right angles to the surface and to the direction of rolling. Observations taken on this set of planes with other specimens corroborate this result. For example, in the case illustrated in Fig. 5*b* the crystal setting for the same maximum was  $165.5^{\circ}$  with the same surface zero and in two other cases the figures were  $163^{\circ}$  and  $168^{\circ}$ . The figures are in agreement with one another within the limits of accuracy of experiment.

It will be convenient to measure the angles of the other planes, fixing this (111) plane as zero. Starting from this plane then, we have in Fig. 5*a* maxima at the following angles:—

$0^{\circ}$ ,  $62^{\circ}$ ,  $118^{\circ}$ ,  $184^{\circ}$ ,  $241^{\circ}$ , and  $297^{\circ}$ .

The last three being separated from the first three by approximately  $180^{\circ}$ , are the reflections from the "back surfaces" of the same sets of planes.

(B) *Rotation of specimen about horizontal axes.*—The specimen was mounted on a frame capable of rotation about two axes perpendicular to each other and to the axis of the spectrometer; one of these axes (A), Fig. 7, was coincident with the direction of rolling and therefore perpendicular to the (111) planes occurring at  $0^\circ$  on the arbitrary crystal scale just mentioned. By setting the specimen in the position to give reflection  $0^\circ$  and rotating it about the A axis, the planes giving the maximum are rotated about their normals and should remain in the reflecting position

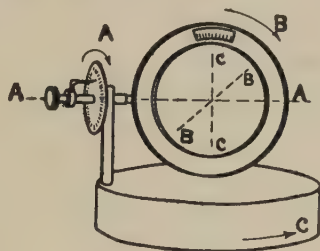


FIG. 7.

during rotation of the specimen. This was found to be the case, as shown in the following table:—

Reading of A ... ..	$-20^\circ$	$-10^\circ$	$0^\circ$	$10^\circ$	$20^\circ$	$160^\circ$	$170^\circ$	$180^\circ$	$190^\circ$	$200^\circ$
Intensity ... ..	9.8	9.9	10	10	9.1	11.0	11.0	11.1	11.1	11.0
	Exposure 20 secs.					Exposure 30 secs.				

When the reading of A is  $0^\circ$  the surface of the specimen lies in a vertical plane. The intensity of reflection is therefore not sensibly affected by the rotation of the specimen about this axis, but, as the following table shows, it is very sensitive to rotation about the axis B (Fig. 7) perpendicular to the plane of the sheet:—

Reading of B ... ..	$-20^\circ$	$-10^\circ$	$0^\circ$	$+10^\circ$	$+20^\circ$
Intensity ... ..	2.6	6.0	8.6	8.0	5.0

The direction of rolling is horizontal when the reading of B is  $0^\circ$ , the intensity being a maximum when  $B \div 0^\circ$  and  $B \div 180^\circ$ .

During the above readings the crystal table stood at  $168^\circ$ . This was now altered to  $98^\circ$ , i.e., the crystal table was rotated through  $70^\circ$ , the angle between the (111) planes being  $70^\circ 32'$ . The axis B was set at  $0^\circ$ , so that the direction of rolling was horizontal and readings were taken as the specimen rotated about the A axis. Two very intense maxima, corresponding to readings of A equal to  $-5^\circ$  and  $+185^\circ$  were observed, the relevant readings being as follows:—

Reading of A ... ..	$-65^\circ$	$-40^\circ$	$-23^\circ$	$-10^\circ$	$0^\circ$	$10^\circ$	$20^\circ$	$30^\circ$
Intensity ... ..	6.2	9.3	9.5	14.0	17.4	11.1	6.5	6.3
Reading of A ... ..	$150^\circ$	$163^\circ$	$170^\circ$	$180^\circ$	$190^\circ$	$200^\circ$	$220^\circ$	$240^\circ$
Intensity ... ..	10.6	11.2	14.6	24.0	26.3	20.0	13.9	9.1



This means that if the first maximum occurring at  $A \div 0^\circ$  is due to planes inclined at  $+a^\circ$  to the surface, the second ( $A \div 180^\circ$ ) is due to planes inclined at  $-a^\circ$  to the surface. Or, in other words, there are two sets of crystals in the material, the one being the optical image of the other in the plane of rolling. Further, it appears that the position of best reflection is again with the surface of the sheet in a vertical plane—so that the axis of the spectrometer must be parallel to the line of intersection of two (111) planes, i.e., to the diagonal of a cube face.

*Discussion of the results.*

The foregoing results indicate that the crystals in the rolled specimens tend to set themselves with a cube diagonal in the direction of rolling and the diagonal of a cube face in the surface perpendicular to the direction of rolling. This arrangement brings a (211) face into the surface of the sheet. Fig. 8 will make this clear;

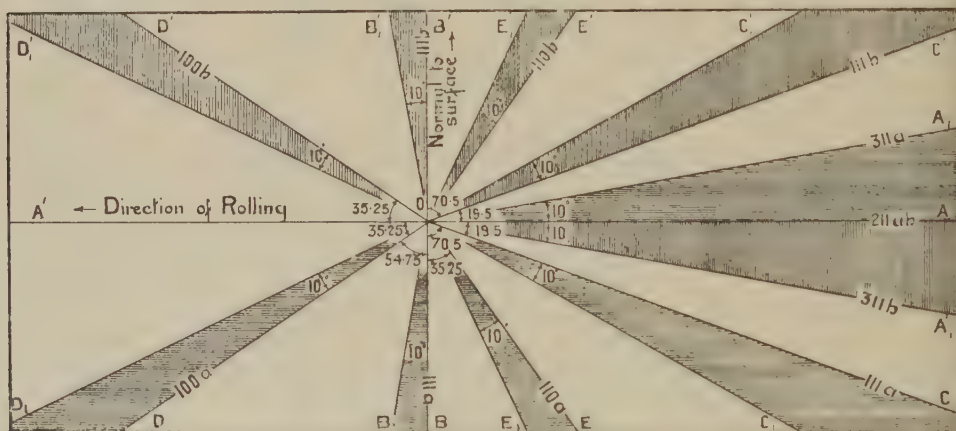


FIG. 8.

in it  $AOA'$  represents the direction of rolling,  $BOB'$  the normal to the surface of the specimen. The axis of the spectrometer in the experiments just described passes through  $O$  and is perpendicular to the plane of the diagram. The line  $OB$  represents the (111) plane at  $0^\circ$  which we have found to be perpendicular to the plane of rolling. There will then be a (111) plane, which cuts the plane of the diagram in the line  $OC$ , the angle  $BOC$  being  $70^\circ 32'$ . From what has just been said there will also be crystal planes which are the reflections of these in the surface of the specimen—so we put lines  $OB'$  perpendicular to  $A$  and  $A'$  and  $OC'$  inclined at  $70^\circ 32'$  to  $OB'$ . We then have the (111) planes occurring at the following angles as the specimen is rotated about the spectrometer axis, starting from  $OB=0^\circ$ ,

$$0^\circ, 70^\circ 32', 109^\circ 28', 180^\circ, 250^\circ 32', \text{ and } 289^\circ 28',$$

while the observed figures are

$$0^\circ, 62^\circ, 118^\circ, 184^\circ, 241^\circ, \text{ and } 297^\circ.$$

The separation of the first two peaks of the observed series differs from the calculated value by  $8.5^\circ$ , which is more than the limit of error of experiment. Several specimens were examined, and great care was taken in each case to get the planes in the

best reflecting position by rotation about the axes A and B (Fig. 7), but the angular separation of the peaks was persistently less than  $70^\circ$ . The following are the figures obtained from several different samples of material:  $62^\circ$ ,  $63^\circ$ ,  $62^\circ$ ,  $62^\circ$ ,  $59^\circ$ ; the last two figures being obtained with the rays confined by a circular aperture of 3 mm. diameter placed near the crystal slit and situated 9 cms. from the bulb slit, the rays in the first case passing through the centre, and in the second case near to the edge of the material. The observations themselves are liable to an error of about  $\pm 2^\circ$ , so that there is no doubt the angle between these peaks is not greater than  $65^\circ$ .

It was observed from the curves which established this fact that the peak given by reflection from the (111) plane perpendicular to the plane of rolling was always about twice as wide as the peaks from the other (111) planes. This is shown in Fig. 5a

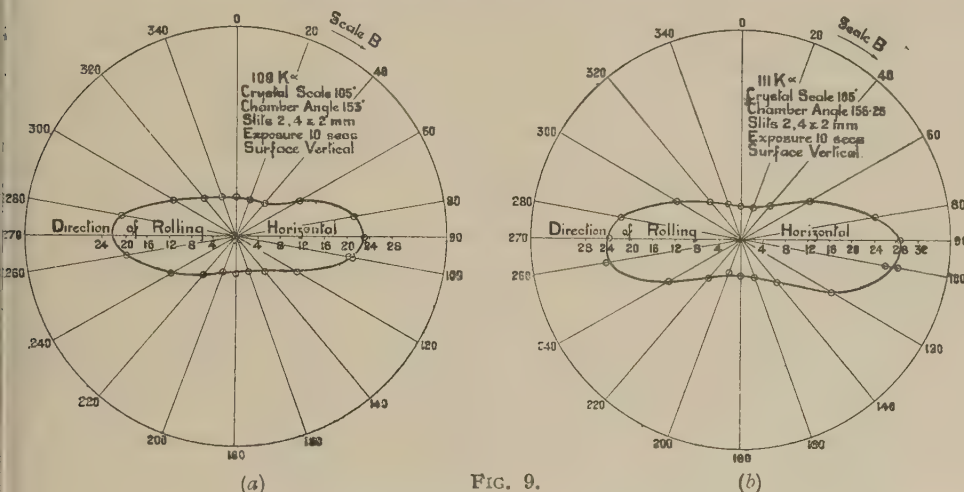


FIG. 9.

and Fig. 10b. The width of the peak being taken at half its height, we have for the widths of the peaks in Fig. 5a, starting from the left,

$11^\circ$ ,  $23^\circ$ ,  $11^\circ$ ,  $14^\circ$ ,  $23^\circ$  and  $10^\circ$ ,

and in Fig. 8b,  $12^\circ$ ,  $20^\circ$  and  $10^\circ$ .

The central peaks are due to the reflections from planes whose traces on Fig. 8 are the lines  $OB$  and  $OB'$ . Calculations shows that a (311) plane belonging to the same zone cuts the plane of Fig. 8 in the line  $OA_1$ , inclined at  $10^\circ$  to  $OA$ , and its reflection in the plane of the specimen is the line  $OA_1'$ , the former belonging to the set of crystals "a" and the second to the set "b," which is the reflection of "a" in  $OA$ . Since the reflection from (311) is particularly intense in the surface of the sheet, let us suppose that the set "a" deviates from the ideal position considered above by  $10^\circ$ , so as to bring its (311) plane into the surface, and that the set "b" also deviates by  $10^\circ$  in the opposite direction. The areas in which the various planes will be localised are shaded horizontally for the "a" set and vertically for the "b" set in Fig. 8, and it will be seen that the planes whose mean position is  $BOB'$  diverge  $10^\circ$  on either side of that line, while for the other lines, such as  $OC$ , the divergence is in one direction only. For  $OC$  it is towards  $OB$ , and for  $OC'$  away from  $OB$ , which

is precisely the effect observed in the measured angular distances between these peaks, the  $OC$  peak occurring  $8^\circ$  too close to  $OB$  and the  $OC'$  peak  $9^\circ$  too far from  $OB$ .

Assuming now that the observed peaks represent the centres of the shaded areas

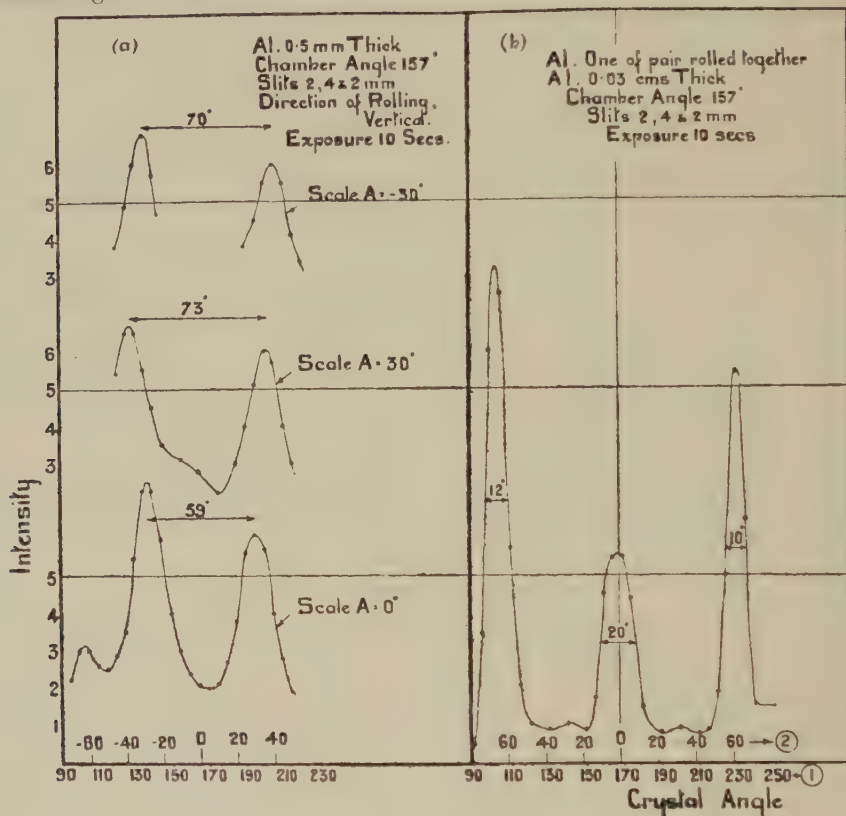


FIG. 10.

of Fig. 8, the following table shows the agreement between the positions of the observed peaks and the positions in which they would be expected from Fig. 8.

Calculated.		Observed.	
Fig. 8.	Fig. 5a.	Fig. 10b.	Another specimen.
0	0	0	0
65	62	63	63
115	118	(115)*	116
180	185	(180)*	(180)*
245	240	(243)*	(243)*
295	294	295	295

\* The figures in brackets are inferred from those observed by the addition of  $180^\circ$ .

Fig. 6 is analogous to Fig. 5a, but in the former the ionisation chamber was set to receive the rays reflected from the (100) (Fig. 6a) and (110) (Fig. 6b) planes. In

comparing the positions of the planes as observed with those to be expected from the scheme illustrated in Fig. 8, we have to start from the same scale reading ( $166^\circ$ ) as for the (111) planes, and add to the figure so found the difference between the angles of reflection for (111) and those for the planes considered. We have

$$\theta_{111}=8.7^\circ, \theta_{100}=10.1^\circ \text{ and } \theta_{110}=14.4^\circ.$$

So to the observed figures, starting from  $166^\circ$  as zero, we must add  $1.4^\circ$  for the (100) and  $5.7^\circ$  for the (110) planes, or to the limits of accuracy required  $1^\circ$  and  $6^\circ$  respectively. The following table shows the results of the comparison of the observed (100) reflections with those expected:—

Observed (Fig. 6a).	Observed + $1^\circ$ .	Calculated.
$0^\circ$	$1^\circ$	(111K $\alpha$ )
$32^\circ$	$33^\circ$	(220K $\beta$ )
$59^\circ$	$60^\circ$	$60^\circ$
$120^\circ$	$121^\circ$	$120^\circ$
$150^\circ$	$151^\circ$	(220K $\beta$ )
$185^\circ$	$186^\circ$	(111K $\alpha$ )
$212^\circ$	$213^\circ$	(220K $\beta$ )
$240^\circ$	$241^\circ$	$240^\circ$
$300^\circ$	$301^\circ$	$300^\circ$
$328^\circ$	$329^\circ$	(220K $\beta$ )

The suggested arrangement evidently accounts satisfactorily for the four larger peaks of Fig. 6a. The small peaks at  $0^\circ$  and  $185^\circ$  are undoubtedly due to stray reflections from the (111) planes which occur at these angles (Fig. 5a). So we are left with peaks at angles of  $33^\circ$  and  $151^\circ$  with *OB* to be accounted for, the intensity of these being but one-tenth of that of the other four. The larger peaks are represented in Fig. 8 by the lines *OD* and *OD'*, and are situated at the middle of the shaded areas shown in that diagram.

Turning now to the (110) planes (Fig. 6b), we have the following comparison between the observed and calculated angles:—

Observed (Fig. 6b).	Observed + $6^\circ$ .	Calculated.
$23^\circ$	$29^\circ$	$30^\circ$
( $85^\circ$ )	( $91^\circ$ )	...
( $115^\circ$ )	( $121^\circ$ )	...
( $147^\circ$ )	( $153^\circ$ )	$150^\circ$
( $203^\circ$ )	( $209^\circ$ )	$210^\circ$
$265^\circ$	$271^\circ$	...
$295^\circ$	$301^\circ$	...
$327^\circ$	$333^\circ$	$330^\circ$

Again we are left with two peaks unexplained at angles of  $91^\circ$  and  $121^\circ$  with *OB*. The remaining planes are represented by the lines *OE* and *OE'* in Fig. 8, and the agreement between the suggested arrangement and the observed position of the planes is again good.

We notice that (110) planes occur at angles of  $29^\circ$  and  $333^\circ$ , which are very close to the two unexplained peaks at angles of  $33^\circ$  and  $329^\circ$  in Fig. 5a. The angle of reflection from (100) planes for *K $\alpha$*  radiation is  $10.1^\circ$ , and from (110) planes for *K $\beta$*  is  $12.7^\circ$ , the difference  $2.6^\circ$  being comparable with the angular divergence of the



incident beam of X-rays. It would, therefore, be possible for  $K\beta$  radiation reflected from (110) planes to enter the chamber slit even when that was set to receive  $K\alpha$  radiation reflected from (100) planes. The point was tested by placing a zirconia filter in front of the ionisation chamber, and the result is shown in the upper curve of Fig. 6*a*. The third peak is quite distinct, but the second and fourth have disappeared, there being no variations in the region where they were expected that cannot be ascribed to experimental error. All the maxima of Fig. 6*a* have now been accounted for, and we have now to explain the presence of the peaks at angles of  $91^\circ$  and  $121^\circ$  in Fig. 6*b*, when the chamber was in the position to receive the (110) reflections.

It appeared possible that part of these two peaks might be due to scattered radiation, since the minima in Fig. 6*b* occur at points where the metal plate is parallel to the incident and reflected beams respectively. The upper curve in Fig. 6*b* shows the effect obtained when a plate of glass 2 mm. thick was substituted for the metal plate on the spectrometer table. Minima are observed in the places where the absorption is evidently greatest, and maxima occur sensibly at the same angles as for the metal plates. The second and smaller unexplained peak is probably entirely due to this effect. The first must be partly due to the same effect, partly due to  $K\beta$  radiation reflected from (311) planes parallel to the surface, and partly due to reflection of  $K\alpha$  radiation from the (110) planes, which with the suggested crystal orientation are inclined at  $30^\circ$  to the vertical (spectrometer axis), and no doubt deviate from this ideal position to some extent.

Further experiments were carried out on the reflections from (100) and (111) planes with a view to ascertaining the effect of scattering. In the case of (100), for example, the crystal table was rotated until the (100) plane giving the first peak on the left in Fig. 6*a* was in the position to reflect the  $K\alpha$  radiation, the chamber being situated in the proper position (reading on scale of chamber 153) to receive the (100) reflection. The specimen was rotated in its own plane and readings taken at intervals of  $20^\circ$  ( $10^\circ$  near the maxima) on the B scale. The results are shown in Fig. 9*a*. It will be observed that two maxima appear, separated by  $180^\circ$  in accordance with the arrangement of planes shown in Fig. 8, and that the intensity of these maxima is about three times that of the radiation scattered into the chamber when the specimen is in the other positions. Similar effects are shown in Fig. 9*b* when the reflections from (111) planes were examined.

The specimen used to obtain the curve in Fig. 5*a* (0.5 mm. thick) was rotated in its own plane until the direction of rolling was vertical. The ionisation chamber was set to receive (111) reflections and the crystal table rotated, the readings being taken at  $5^\circ$  intervals as for the curve in Fig. 5*a*. The result is shown in Fig. 10*a*. Reflections from (111) planes occur at angles  $-29^\circ$  and  $+30^\circ$  from a vertical plane perpendicular to the surface of the material. There is very little trace, if any, of (111) reflections from planes perpendicular to the surface.

The observed reflections agree with those to be expected from the arrangements suggested in the present Paper, according to which we are in the above experiment rotating the cube about the cube diagonal. The (111) planes are then inclined at  $20^\circ$  to the axis of the spectrometer, and will come into the reflecting position at  $60^\circ$  intervals, which is within  $1^\circ$  of the figure observed.

The specimen was now rotated about the axis A (Fig. 7) until the direction of rolling was  $30^\circ$  to the vertical. The peaks separated to  $73^\circ$ , and at  $-30^\circ$  to the

vertical the value of  $70^\circ$  was obtained as shown in Fig. 10a. These observations again agree with the reflections to be expected from the crystal orientation suggested here. The theoretical separation of  $70^\circ 32'$  is obtained because the planes at which reflections occur belong to the same set of crystals (either set "a" or set "b").

This experiment shows that the arrangement of crystals suggested by Mark and Weissenberg does not exist to any appreciable extent in aluminium rolled from 1 cm. to 0.05 cm. thickness.

The above results, which were exclusively obtained with the ionisation spectrometer, confirm the conclusions of Wever.

## II. MEASUREMENTS BY THE PHOTOGRAPHIC METHOD.

It was considered advisable to examine the problem further by the photographic method, in view of the discordant results obtained by previous observers with this method of analysis. The rotating crystal method was used, the specimen of foil 0.01 cm. thick being rotated during exposure about the direction of rolling, the transverse direction and the foil normal respectively. The three photographs so obtained are shown in Figs. 11, 12 and 13, radiation from a copper anticathode being employed in each case. If we take a line on the photograph perpendicular to the axis of rotation, and call the angle between this line and the line joining one of the diffraction spots to the centre spot  $\alpha$ , then

$$\sin \alpha = \frac{\cos \varphi}{\cos \theta}$$

where  $\varphi$  is the angle between the axis of rotation and the normal to the plane giving the spot, and  $\theta$  is the glancing angle of the X-rays. It is, therefore, possible to calculate the values required by the arrangements of Mark and Weissenberg, and by that of Wever. This has been done, and the results are shown graphically for comparison with the photographs.

In Fig. 11 we have a photograph taken with the specimen rotating about the direction of rolling. The type of picture to be expected if the axis of rotation is within  $8^\circ$  of a [112] direction is shown in Fig. 14a, while Fig. 14b is constructed on the assumption that the axis lies anywhere between [111] and [112]. The chief difference between the two calculated diagrams is that in the latter the spots tend to run together. On the photographic plate the reflections of 100 planes seem to be a continuous band from  $\alpha=26^\circ$  to  $\alpha=64^\circ$ , with a very intense spot in the region covered by the smaller values of  $\alpha$ . The photograph can be equally well interpreted by either arrangement.

Fig. 12 is a photograph taken during rotation of the specimen about the transverse direction. Fig. 15a is calculated from Mark and Weissenberg's data, the axis of rotation lying between [201], [111] and [021]. Fig. 15b is constructed for the case when the axis lies between [110] and [221]. The position of the reflections from (100) is in agreement with the latter arrangement.

The former requires this spot to lie in a position for which  $\alpha=35 \pm 4^\circ$ , the latter requires  $\alpha=47 \pm 3$ , while the observed value is  $46 \pm 10$ , the greater width being due to the divergence of the X-ray beam. The arrangement of Mark and Weissenberg does not explain the position of the spots on this photograph.

The photograph in Fig. 13 is taken with the specimen rotating about the foil normal. It may be compared with Fig. 14a, which shows the theoretical distribution for rotation about a  $[11\bar{2}]$  direction.

The photographs agree with the results obtained with the spectrometer, and confirm the results of Wever.



FIG. 14.

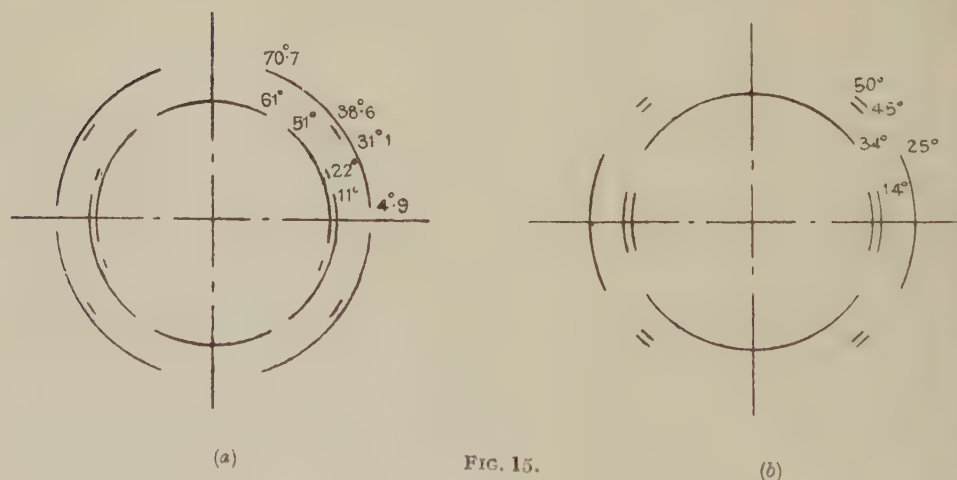


FIG. 15.

#### CONCLUSIONS.

When a cast specimen of aluminium containing a number of comparatively large crystals orientated at random throughout the body of the material is rolled, the crystals break up into a large number of minute crystals. As the thickness of the material is progressively diminished, the small crystals tend to take up a definite orientation, each crystal having a cube diagonal in the direction of rolling and a  $(211)$  plane in the plane of rolling.

Two sets of crystals exist in the material after rolling, the one set being the optical image of the other in the plane of rolling.

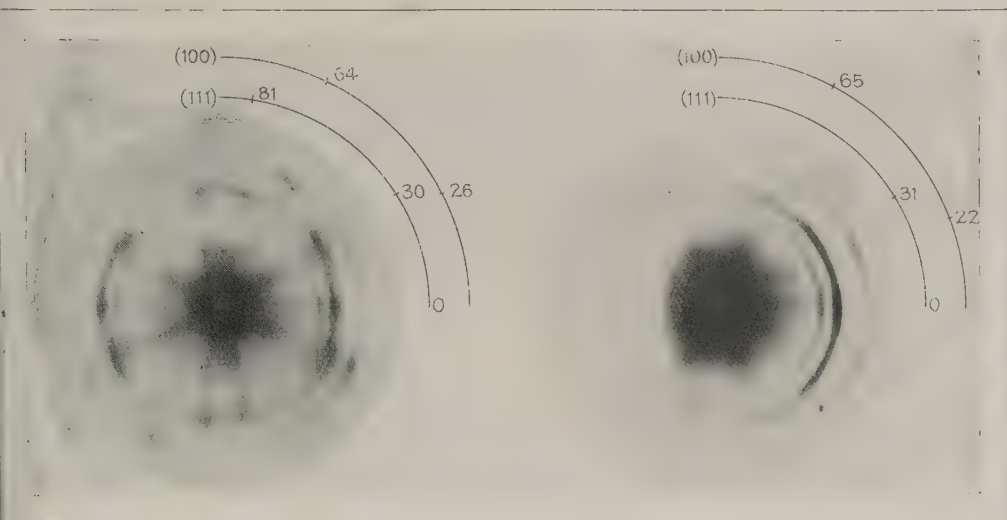


FIG. 11.—X-RAY PHOTOGRAPH OF ALUMINIUM FOIL, TAKEN DURING ROTATION OF SPECIMEN ABOUT THE DIRECTION OF ROLLING.

FIG. 13.—X-RAY PHOTOGRAPH OF ALUMINIUM FOIL, TAKEN DURING ROTATION OF SPECIMEN ABOUT THE FOIL NORMAL.

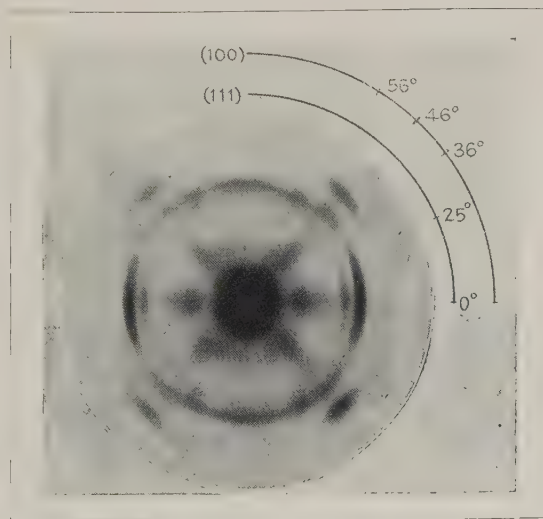


FIG. 12.—X-RAY PHOTOGRAPH OF ALUMINIUM FOIL, TAKEN DURING ROTATION OF SPECIMEN ABOUT THE TRANSVERSE DIRECTION.









FIG. I (*Discussion*).



FIG. II (*Discussion*).



FIG. III (*Discussion*).



FIG. IV (*Discussion*).

The observations obtained by the ionisation spectrometer indicate that the type of the space lattice remains unaltered, and that the parameter of the material in the severely worked condition does not differ from that of the annealed material by more than 0.5 per cent. On the other hand, the diffraction spots on the photographs are rather broad. This would suggest either that the parameter is subject to variations—in other words, that the lattice is distorted—or else that the crystals are of colloidal dimensions. The experiments described above are probably in themselves insufficient to decide between these two alternatives. It is to be observed, however, that deformation which takes place by “slip” produces subdivision of the crystals, and may or may not be accompanied by linear deformations. Determinations of the density of the material as cast and in various conditions after rolling showed no variations greater than 1 part in 1,000. This indicates that the average lattice constant does not on the whole differ from the normal by more than 1 part in 3,000, and lends support to the determination by means of the spectrometer. It does not, however, dispose of the possibility of the material being self-strained in such a manner that parts of it are compressed while others are extended.

#### DISCUSSION.

Miss L. ELAM discussed the relative merits of the photographic and the ionisation-spectrometer methods. The latter method she considered somewhat unreliable for the present purpose, unless elaborate precautions be taken to move the specimen about both vertical and horizontal axes. If the reflecting planes be not accurately vertical, reflexions may occur which fail to enter the chamber and so pass unnoticed, and in any case the intensity is so much affected by the inclination of the specimen that little importance can be attached to the maximum and minimum values obtained. Thus the flattening of the peaks in Fig. 3 may be due to this cause, the orientation of the crystals being altered in the vertical plane by rolling; some of them may become placed in a more favourable position for affecting the chamber. This suggestion is borne out by the photographs in the Paper, since they show an almost continuous ring of scattered radiation where the ionisation chamber gives indications corresponding to only a few degrees of this ring.

Prof. F. L. HOPWOOD said that both speakers had avoided referring to the amorphous surface layer. Had the assumption that such a layer exists been abandoned?

Dr. E. A. OWEN, in reply, said that he disagreed with Miss Elam. He considered that the spectrometer method was as reliable as, if not in some respects superior to, the photographic method. In the latter the photographs showed reflections from a number of crystal planes in the specimen, but they gave no indication as to the orientation of the specimen when the reflections occurred. In the spectrometer method, as used here, the specimen could be turned in any direction so that the reflections from any desired set of planes in the specimen could be examined. He was of opinion, however, that the most satisfactory procedure was to employ the two methods in conjunction, as had been done in the investigation described in the Paper, in which an attempt was made to decide between two discordant results obtained by the photographic method. No indication of an amorphous layer had been found in these experiments.

Dr. E. V. PULLIN (communicated): It may be of interest if I contribute one or two spectrograms which serve to illustrate Dr. Owen's remarks. These were obtained some five or six months ago in my laboratory by Dr. Gilbert West. Fig. I is a spectrogram of aluminium before strain taken by the reflection method and using rhodium radiation. Fig. II is a similar spectrogram taken after the aluminium had been strained. It will be seen that the speckled appearance, indicating large crystals, has disappeared in Fig. II. Figs. III and IV are spectrograms taken by the transmission method using unfiltered Tungsten radiation. In Fig. III large crystals are again indicated by the spotted appearance. In Fig. IV this has disappeared, indicating once more the break-up of the large crystals into smaller ones. The figure also illustrates that although broken up, the lattices of the crystal fragments are preferentially oriented.



## XVIII.—THE SPREADING OF ONE LIQUID ON THE SURFACE OF ANOTHER.

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*Received October 30, 1925.*

*(Communicated by Mr. EDWIN EDSER, A.R.C.S., F.Inst.P.)*

## SUMMARY.

The Paper gives an account of preliminary investigations into the spreading of liquids on mercury. Water and solutions of a number of inorganic substances are tested.

Purest "conductivity" water in the presence of air is found to spread very slowly on a clean mercury surface; the spreading is greatly accelerated by traces of acid in solution, and totally inhibited by traces of alkali.

All the neutral salts tested, even chlorides of mercury and silver, are found to produce rapid spreading. By varying the concentration of the solution the rate of spreading is controlled; the phenomena are described and photographed.

All acid solutions tested spread rapidly, probably reacting chemically with the mercury. One part of hydrochloric acid in ten million of water definitely accelerates spreading. A drop of very dilute acid spreads rapidly to cover a definite area and stops, any further spreading being as slow as that of water. The area covered during the rapid stage depends on the nature of the acid; it is proportional to the number of acid molecules present, and is larger than would be expected if a monomolecular layer of the appropriate salt were formed on the mercury surface.

Drops of certain alkaline solutions, notably ammonia, are found to spread after a period of delay, the spreading being due to carbon dioxide absorbed from the air.

Electrostatic fields up to 4,000 volts/cm. applied perpendicular to the surface produce no visible results. Placing a platinum wire from one terminal of a battery in the mercury and from the other terminal in the drop, and applying small voltages, causes spreading even in alkalis if the mercury be positive, and prevents spreading even in dilute acids if the mercury be negative.

Increasing the field beyond that necessary to prevent spreading (mercury negative) sets up an oscillation, the drop spreading till it breaks contact with the terminal, and then contracting. An E.M.F. of 400 volts was required to produce this effect with a drop of conductivity water.

A method of photographing films on the surface of mercury is described. By the same means a photograph is obtained showing a drop of oil spreading on a water surface. The spreading film is preceded by a well defined ridge, probably that observed by Osborne Reynolds, but apparently by none of the more recent writers.

The Paper concludes with a description of a ridge that may be observed under certain conditions when water is draining from a sheet of perfectly clean glass.

## I. INTRODUCTION.

IN recent years a number of investigations by different inquirers have dealt with the spreading of organic liquids on the surface of water, and particularly with the nature of the molecular surface film in its condition of extreme tenuity.\* The corresponding phenomena when mercury is substituted for water have not received an equal amount of attention. With a view to ascertaining what specific differences might exist in the case of the two liquids, and particularly in order to test the correctness of the view regarding the part played by chemical affinity in the phenomena

\* Langmuir, *Jour. Am. Chem. Soc.*, September (1917). Harkins, *Jour. Am. Chem. Soc.*, p. 354 (1917). Adam, *Proc. Roy. Soc., A*, 99, p. 336; and *A*, 101, p. 452. Labrousse, *Ann. de Physique*, 14, p. 164.

of spreading, the investigation hereunder described was proposed to me by Prof. Kerr Grant in 1922, and has been proceeding since that date.

The Paper contains an account, which is almost purely descriptive, of the more important results which have been obtained. No comprehensive theory has yet been found to cover all the observed facts, which appear to be as difficult to explain on the basis of Langmuir's chemical theory of spreading as on that of the customary physical theory.

## II. PREPARATION OF MATERIALS.

The difficulty of obtaining a perfectly clean mercury surface can only be realized by those who have attempted to work with this liquid on surface tension phenomena. No ordinary "chemically pure" distilled mercury is of the slightest use. After trying several of the usual methods of cleaning mercury without success, it was found that by distilling in a hard glass still in a slow air current, and then shaking thoroughly with a mixture of sulphuric acid and potassium bichromate, it was possible to obtain mercury having a satisfactory surface.

This method gave mercury which henceforth, so long as it received no fatty contamination, only required to be washed and passed through a separating funnel in order to give consistent behaviour.

Mercury is exceedingly liable to receive contamination from glassware. In some of the experiments glass dishes 3 in. in diameter and  $\frac{1}{4}$  in. deep were used. Three of these were washed in strong chromic acid solution for some hours, then boiled for some time in distilled water and rinsed in pure cold water. They maintained a perfect unbroken water film until dry, yet when filled with clean mercury from the same bottle they showed distinct characteristics; a drop of tap water placed on mercury in the first dish spread completely; there was only a slight spread on mercury in the second dish, and none at all in the third.

Prolonged treatment finally brought the dishes to a uniformly satisfactory state, after which they remained clean if reasonable care were exercised.

## III. WATER ON THE SURFACE OF MERCURY.

There are still differences of opinion as to the behaviour of pure water on a mercury surface. The observations of Harkins\* agree in a general way with those made in these experiments.

In the presence of air, a drop of ordinary distilled water placed on a fresh mercury surface spreads slowly and uniformly, retaining its circular form. The spreading continues until, under the processes combined with evaporation, the drop passes through a stage showing film-colours, and vanishes by evaporation. (This forms a simple test of the perfection of the mercury surface.) If this has not involved too long an exposure of the mercury surface, a second drop will behave in a similar manner. Harkins\* states that a mercury surface exposed to air rapidly becomes contaminated by a film of water-vapour, and suggests this as the reason for water not spreading on a surface which has been exposed for any length of time. It is found, however, that a drop of water will spread on the surface after a previous drop has spread and evaporated, and also after the mercury has been exposed in an atmosphere saturated with water-vapour until a visible film has condensed on it,

\* *Journal Am. Chem. Soc.*, December (1920), and December (1922).

and the surface is then allowed to dry without disturbance. In the presence of a saturated atmosphere, however, a drop of water does not spread. Moreover, if the mercury surface be contaminated by the addition of one-tenth the amount of oil necessary to give a monomolecular layer over it, the water is prevented from spreading.

A drop of tap-water spreads many times faster than distilled water. The purer the water the more slowly it spreads. High-grade conductivity water was prepared by re-distilling conductivity water in a pyrex all-glass still and condenser. This water is found to spread uniformly taking possibly 5 minutes for a drop to spread to a disc 5 cm. in diameter. Water from a soft glass still did not spread, and this was found to be due to traces of alkali present even after steaming out for some days. (See Section VI.)

In an atmosphere containing a high percentage of  $\text{CO}_2$  a drop of conductivity water spreads rapidly after a few seconds. A small percentage of  $\text{NH}_3$  in the atmosphere entirely prevents spreading.

The increasing slowness of spread with increasing purity of water makes it at least probable that pure water spreads on the surface of mercury only in virtue of the presence of dissociated molecules. Evidence given later shows that the presence of the H-ion accelerates spreading while the OH-ion retards or inhibits it.

#### IV. SOLUTIONS OF INORGANIC SALTS.

The addition of acid or neutral salt to water greatly increases its rate of spreading on mercury. One part NaCl in 100,000 parts water markedly increases the rate and the effect of one part HCl in ten millions of water is quite evident.

If the spreading is not too rapid, and the mercury is in perfect condition and free from vibration, the drop maintains a circular form having a ridge around the periphery. This ridge then develops irregularities which slowly resolve themselves into droplets. The phenomenon appears to be of the same nature as that observed by Devaux\* when benzine spreads on slightly contaminated water, but here the process can be made to take place quite slowly and the changes studied in detail.

The very general occurrence of this ridge at the edge of the spreading liquid appears to support the theory of squeezing action as the cause of spreading.† This is particularly the case with very dilute HCl in which one would expect the active cause of spread (HCl) to be less concentrated at the advancing periphery of the drop than elsewhere owing to its removal by reaction with the mercury. (See Section V.) The centre of the spreading disc where the HCl is more concentrated might then exert a squeezing action forcing the liquid to spread outward as indicated by the ridge. The difficulty here as in other cases is to picture the mechanism by which the addition of one molecule of HCl to some millions of water-molecules is going to greatly increase the squeezing action between the water and mercury.

Photography of water films possibly less than one thousandth of an inch in thickness on a mercury surface presents difficulties, but by the method described in Section VIII, the accompanying plates (Nos. 1-10) were obtained. These give an idea of the phenomena occurring during spreading, but each picture represents a different drop as it was not possible to obtain a series showing the stages from a single drop. Moreover the pictures are foreshortened, circular drops appearing

\* Jour. de Physique, p. 698 (1912).

† Edser: Fourth Report on Colloid Chemistry, B.A.A.S.

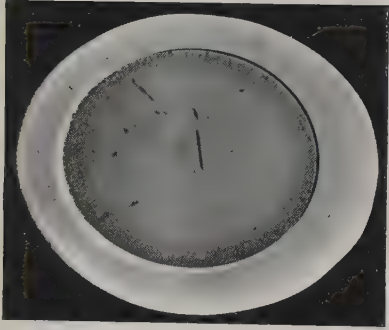


PLATE 1.

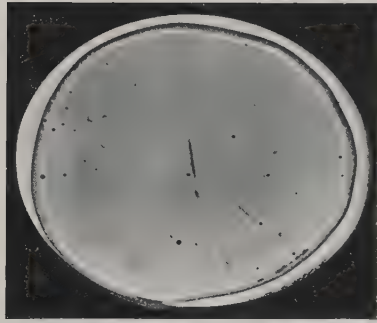


PLATE 2.

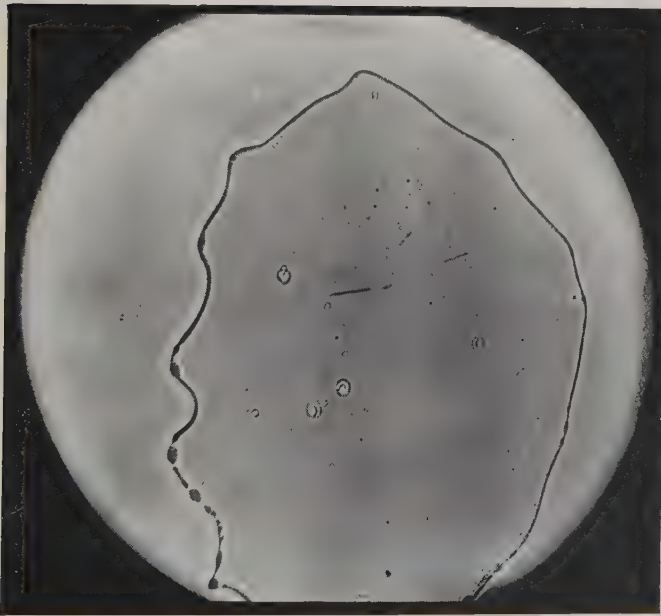


PLATE 3.







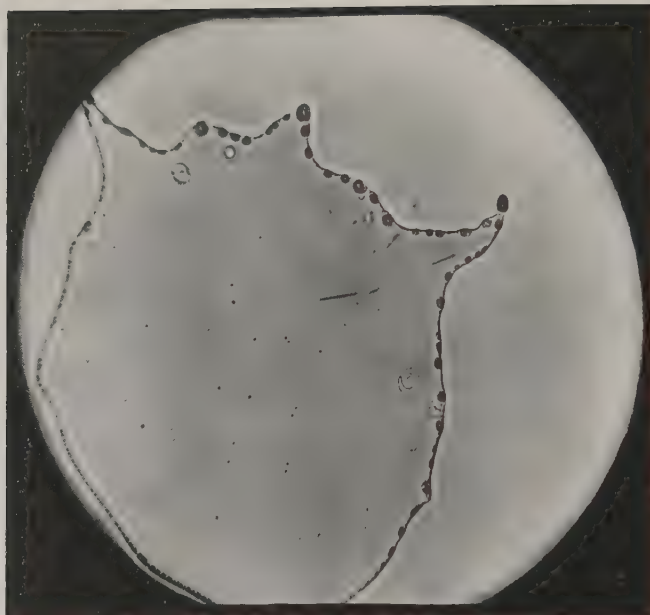


PLATE 4.

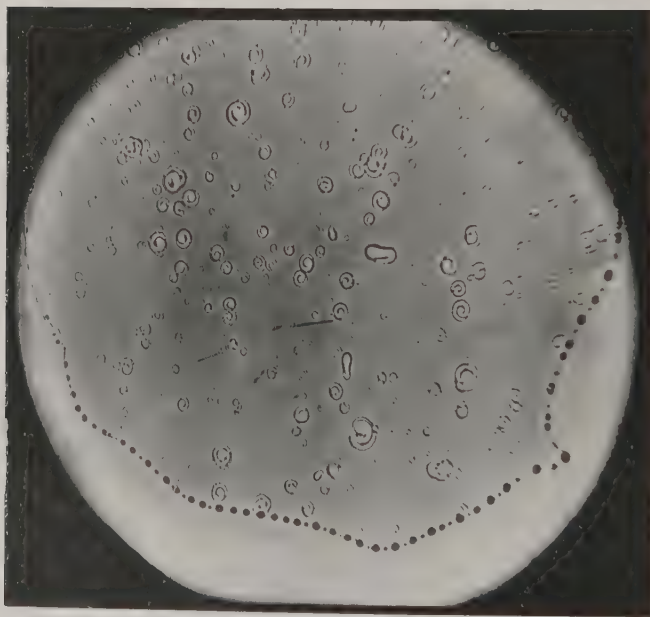


PLATE 5.

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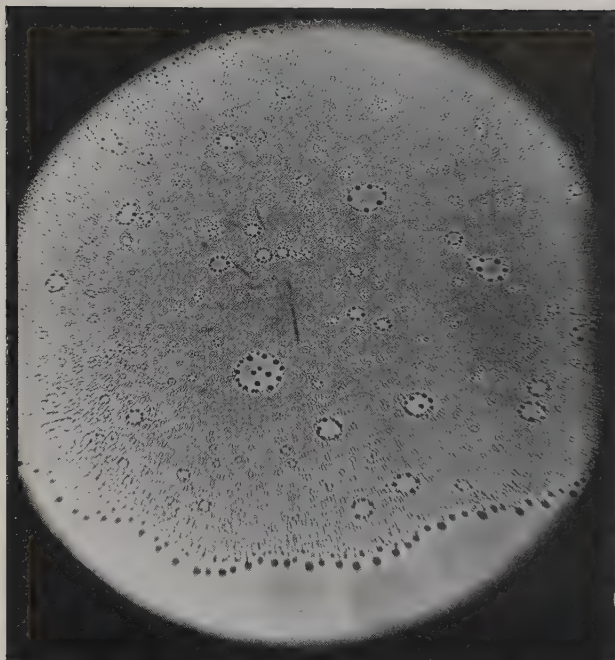


PLATE 6.

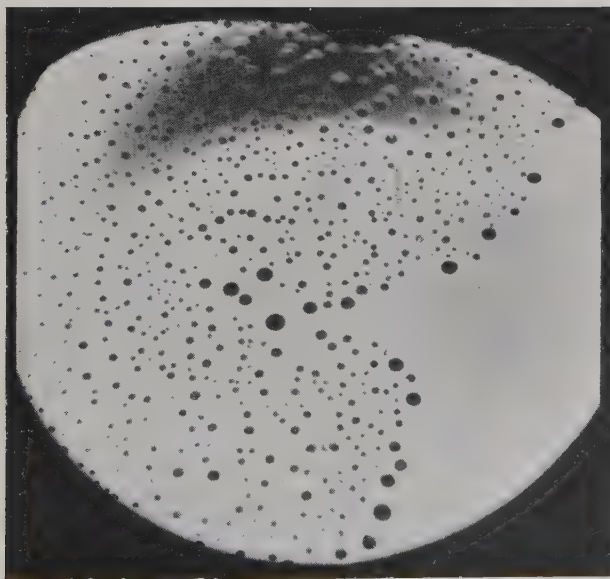


PLATE 7.

[To face page 151]







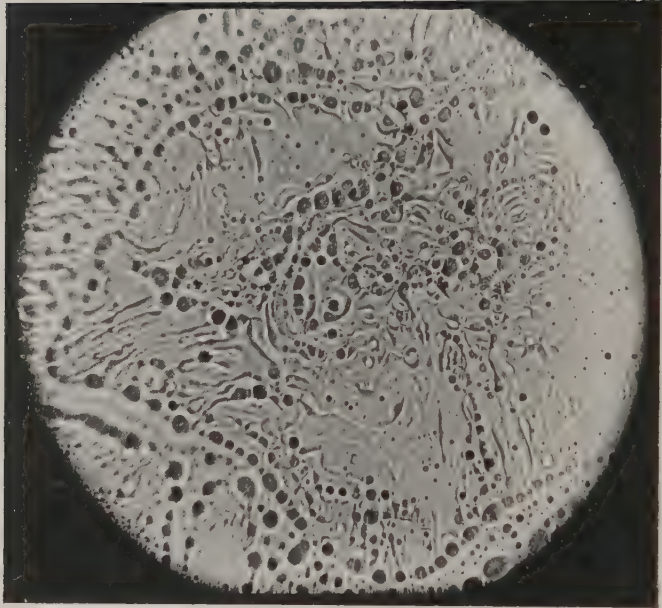


PLATE 8.



PLATE 9.

[To face page 151]

as ellipses. The amount of foreshortening is shown by Plate No. 1, which represents a drop of conductivity water that has spread to a circle 3.5 cm. in diameter.

All the plates show certain markings near the centre which are due to flaws in the large lens of the optical system being reflected in the mercury surface.

Plates Nos. 2-7 represent drops of 0.05 normal solution of NaCl. The peripheral ridge is shown (Nos. 2-4), the development of instabilities in this ridge finally giving a surrounding ring of droplets (Nos. 4, 5 and 6). The solution then pulls away from this ring of drops as shown in No. 6. The film develops further instabilities and resolves into a series of droplets more or less evenly distributed over the surface as shown in No. 7.

In obtaining these plates the mercury surface was exposed to atmospheric dust and a curious phenomenon was observed. Each dust mote landing on the very thin liquid film commences to rotate, some at high speeds, but more usually taking one or two seconds per rotation. This forces the liquid of the film out into a spiral-shaped ridge. Plates Nos. 3, 4 and 5 show progressive stages in the formation of these spirals. No. 6 shows the final stage in which each spiral has developed into a ring of droplets.

Plates Nos. 8 and 9 show the typical appearance when a more concentrated solution is used and dust is excluded. Within the outer ring of droplets (not shown in Plates) corrugations appear all over the surface (No. 8). These rapidly resolve themselves into drops (No. 9). Then as evaporation proceeds the salt crystallizes out, minute crystals forming and dashing hither and thither before attaching themselves to the crystal pattern. Beautiful opalescent colours are seen as the layer of crystals acquires the requisite thickness.

The velocity of spread is high for concentrations greater than one part salt in 20,000 of water. Below this value the rate of spread decreases rapidly.

A solution of ammonium carbonate spreads with great speed to the edge of the mercury and immediately contracts to a drop again, film colours showing for an instant over the surface after the drop has contracted. A ring of very tiny droplets is left at the outer limit to which the drop spreads. These droplets then each spread and evaporate leaving a film of carbonate over the mercury. As soon as this process is completed the original drop flashes out again throwing off a second ring of droplets. This goes on until the whole surface is covered with a solid deposit of carbonate.

The process here appears to be of the same nature as that observed with certain oils on water, i.e., the solution spreads but becomes unstable and the surplus liquid rapidly collects into a drop again. In the case of some oils on water this condition is then stable but with the solution on mercury the process is repeated. The thin film evaporates and since the ammonium carbonate left behind apparently does not affect the surface tension of the mercury the drop of solution spreads again as soon as evaporation is complete.

By using solutions of different salts a great diversity of effects is shown. No two salts behave in quite the same way, though there are certain broad similarities, solution of salts of a given type (e.g., carbonates), showing certain features in common as distinct from those exhibited by solutions of, say, the chlorides.

A point of interest is that the addition of a minute quantity of carefully washed calomel to conductivity water causes it to spread rapidly. Dr. Cooke, of this University, to whom this fact was submitted, suggests that this may be due to hydrolysis of the dissolved  $\text{Hg}_2\text{Cl}_2$  producing free HCl.



## V. INORGANIC ACIDS.

Hydrochloric acid of concentration as great as 0.01 normal flashes out over the surface and contracts again to a drop, leaving a film of calomel on the mercury. The drop then expands and contracts in an irregular manner wherever it succeeds in sweeping aside or breaking through the calomel on the mercury surface. The movements are strongly suggestive of those occurring in living micro-organisms. When the drop finally comes to rest there is a pale blue film over the mercury surface, and generally further flakes of solid within the drop. Sufficient calomel was collected to identify it by chemical tests.

(a) *Definite Limit to Area of Rapid Spread.*—In working with progressively increasing dilutions of any salt or acid it is found that at a certain point the rate of spread begins to decrease much more rapidly than the concentration. The dilution at which this occurs differs widely for different substances and is much greater for acids than for salts. With acids the effect manifests itself in a very striking way. Thus a drop of very dilute HCl was found to spread to a circle 4 cm.

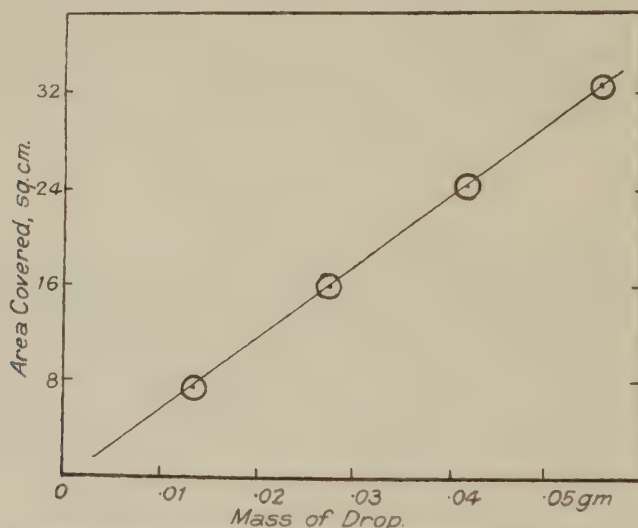


FIG. 1.—AREAS COVERED BY DROPS OF VARIOUS SIZES, USING HCl OF CONSTANT CONCENTRATION.

radius in one second and thereafter to spread as slowly as pure water, taking approximately a minute to increase its diameter by a further 5 mm. The transition point is very definite; using a scale supported just above the mercury surface so as to be reflected in it, it is possible to measure to within 0.5 mm. the diameter of the disc when rapid spreading ceases.

With a given concentration of acid the area covered during the stage of rapid spread is proportional to the mass of the drop. Fig. 1 shows mass of drop plotted against area covered for drops 1, 2, 3 and 4 times the mass of the drop given by the pipette used.

With drops of constant size the area covered is proportional to the concentration. Fig. 2 shows concentrations plotted against areas covered for HCl and HBr using drops of constant size but varying concentration. Thus a drop of HCl

solution spreads rapidly to an area that depends only on the number of acid molecules present in the drop. This relation certainly holds down to a point where the film is less than .001 mm. in thickness. Always there is this rapid spreading and abrupt stoppage, followed by a further very slow spreading except in cases where the film is very thin.

Observations were taken on the areas covered by drops of known mass and concentration for HCl, HBr, and HNO<sub>3</sub>. Solutions of moderate strength in conductivity water were prepared and measured by titration. Then by direct dilution the concentration was reduced to 0.000084 normal.

The pipette used gave drops with an average mass of 0.029 gm. Each drop thus contained approximately  $2.45 \times 10^{-9}$  gm. mol. of acid. In making the observations a reading was taken with each acid in turn and this was repeated until sufficient readings were taken. This assures that differences in area covered by

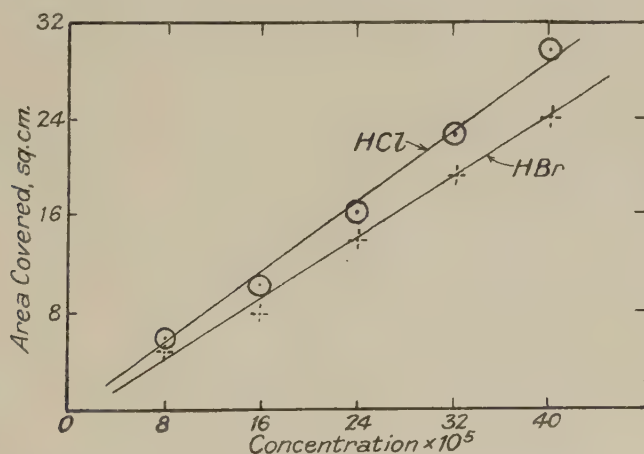


FIG. 2.—AREAS COVERED BY DROPS OF EQUAL MASS BUT VARYING CONCENTRATIONS FOR HCl AND HBr.

different acids were not due to using mercury surfaces of varying degrees of freedom from contamination.

The mean areas covered by a drop of each kind of acid were :—

HNO <sub>3</sub>	...	...	...	16.7 sq. cm.
HCl	...	...	...	15.0 „ „
HBr	...	...	...	12.0 „ „

Taking  $6.06 \times 10^{23}$  molecules per gm. mol. the numbers of acid molecules per sq. cm. of mercury surface when rapid spread ceased were for

HNO <sub>3</sub>	...	...	...	$0.90 \times 10^{14}$
HCl	...	...	...	$1.01 \times 10^{14}$
HBr	...	...	...	$1.26 \times 10^{14}$

Now 1 c.c. of mercury contains approximately

$$\frac{13.6}{200} \times 6.06 \times 10^{23} = 41.2 \times 10^{21} \text{ atoms.}$$

One sq. cm. of mercury surface should, therefore, contain about

$$(41.2 \times 10^{21})^{2/3} = 12 \times 10^{14} \text{ atoms of mercury.}$$

Hence the acid spreads rapidly until it covers an area such that there is only one acid molecule to about ten mercury atoms at the common surface.

Assuming that the spreading is accompanied by chemical action here, as it certainly is at higher concentrations, it seems that only about one-tenth of the atoms in the mercury surface are attacked unless there is a transition layer of very low density at the surface of the mercury. Though the areas covered are consistent to within a few per cent., it is unlikely that a continuous monomolecular layer of mercury compound is formed on the surface, firstly, because of the large area covered per molecule of acid, and secondly, because the bromide occupies considerably smaller area per molecule than the chloride.

There does appear to be a definite connection between the area and the activity of the acid. At such dilutions there would be complete ionization, and hence identical H-ion concentrations, yet acids show these pronounced differences in the extent of spreading. Moreover, heating the mercury to 60°C. causes an increase in the area covered. The heating produces a more rapid spreading and a more pronounced peripheral ridge. After the first drop has evaporated from the hot mercury a second drop will spread. This shows that the surface is almost uncon-



FIG. 3.—WATER ON THE POINT OF FLOWING OVER THE EDGE OF A MERCURY SURFACE.

taminated as would be expected from the small number of molecules of mercury salt formed. It is not possible, however, to repeat the process more than three or four times.

(b) *Spreading stopped by Curvature of Mercury Surface.*—After a drop of water or solution has spread on a mercury surface it is observed that on pouring the mercury from the dish the liquid film invariably collects and travels out on the top of the mercury stream. This is the case even where a considerable amount of solution has been placed on the mercury.

By grinding a shallow depression in a sheet of plate glass and filling with mercury a surface of constant area was obtained, the surface of the mercury being well above the containing dish (see Fig. 3). It was found that the spreading drop never went over the curved edge of the mercury. Even with acid solution in which the velocity of spread may be a thousand times as great as that of water, the solution never goes over the edge. Using a burette, observations were taken of the amount of solution that could be added before it flowed over the edge of the mercury. Conductivity water was found to break and flow over just as the water sheet reached a thickness of 4.5 mm. Dilute acid solution overflowed at the same thickness as nearly as could be determined. Conductivity water was then dropped from a burette on to a freshly-paraffined glass surface and the water was found always to

cover such an area that its depth was very nearly 4.5 mm. It appears then that the addition of an electrolyte to water merely increases the velocity of spread on mercury without causing it to spread further. Moreover, it is the surface tension of the solution and not that of the interface which appears to determine when the solution will flow over the curved edge of the mercury.

A small drop of olive oil or of liquid paraffin, on the other hand, at once spreads completely over the mercury surface, spreading down over the curve as readily as on the plane surface.

#### VI. SOLUTIONS OF INORGANIC BASES.

These solutions do not spread on mercury. Hydroxides of barium, calcium, sodium, potassium and ammonium were tested. The presence of the OH-ion tends actively to prevent spreading, i.e., it does not merely fail to cause it, for a solution of NaCl may be prevented from spreading by the addition of NaOH.

*Action of Atmospheric CO<sub>2</sub>.*—A solution of pure Na<sub>2</sub>CO<sub>3</sub> will not spread, but after prolonged exposure to the air it may spread owing to the absorption of CO<sub>2</sub>. A drop of commercial ammonia fortis placed on mercury shows a violent swirling motion at the periphery, and after a few seconds begins to spread rapidly. Pure ammonia fortis was then prepared by passing NH<sub>3</sub> over caustic potash into conductivity water. A drop of this showed no sign of spreading or of action at the periphery for several minutes. After about five minutes the drop flattens and spreads fairly rapidly. This period of hesitation is found to be consistent and is greater for larger drops and for more dilute solutions. The latter fact shows that the delay is not merely the time required for the drop to lose NH<sub>3</sub> to the air. The spreading is due to a combination of two processes. (1) Loss of NH<sub>3</sub> with consequent reduction in the OH-ion concentration, and (2) the formation of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> by absorption of CO<sub>2</sub> from the atmosphere. The period which elapses before spreading begins is reduced by placing the dish in a current of air containing a higher percentage of CO<sub>2</sub>.

A solution of ammonia was prepared of such concentration that a period of seven minutes elapsed before the drop commenced to spread. Even this long period was found to be constant to within a few seconds. The extreme difficulty of maintaining a clean mercury surface probably renders this impracticable as a means of determining the CO<sub>2</sub> content of the air.

#### VII. EFFECTS OF ELECTRIC FIELDS AND ELECTROLYSIS.

Since spreading appears to be determined by the nature of the ions, it was resolved to try the effects of electric fields in controlling these.

(a) *Static Fields.*—One terminal of a 400-volt battery was placed in the mercury, and the other connected to a small horizontal plate which could be lowered over the mercury. For water and other liquids that do not spread rapidly, it was found that fields up to 4,000 volts/cm. produced no visible differences in the phenomena.

(b) *Closed Circuits.*—The effect of applying various voltages directly across the drop was then tried. One terminal was placed in the mercury and the other (a clean platinum wire) was brought into contact with the drop. With solutions of KOH or NaOH, and the mercury positive, at about 2 volts a slow spreading occurs,



and a grey film (probably oxide or hydroxide of mercury) forms in concentric rings on the surface. Reversing the field causes the surface to clear, while the solution collects once more into a drop. Then, if the voltage is sufficient, the drop spreads again until it pulls away from the platinum wire. It thereupon contracts rapidly to a drop once more, comes into contact with the platinum wire and again spreads, the process repeating itself indefinitely. This alternate expansion and contraction occurs at a point that is definite to within 0.01 volt under given conditions. Just at the critical voltage the drop spreads slowly to an inch or more in diameter, and contracts rapidly on breaking from the platinum point. With a slightly higher voltage the process is so rapid that the oscillation of the drop gives an interruption of the current of sufficient frequency to cause a fluttering sound in a telephone joined in parallel with the drop. With still higher voltages (6-10 volts) the initial spread may be so violent that the drop flies to pieces.

For NaOH and KOH the oscillation sets in at a voltage close to the decomposition voltage, but the actual amount of current passing through the drop appears

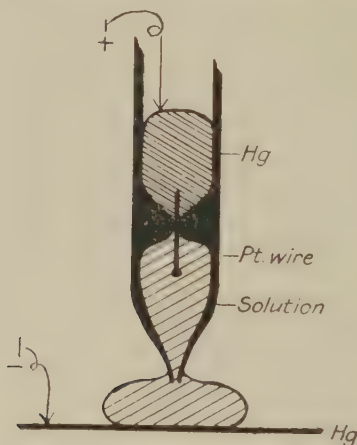


FIG. 4.—METHOD OF USING A -VE TERMINAL, COMPOSED OF THE SAME LIQUID AS THAT IN THE DROP ON THE MERCURY SURFACE.

to be an important factor. Thus a solution of  $\text{NH}_4\text{OH}$  requires a higher voltage to produce oscillation than does a solution of KOH, although the decomposition voltage of the ammonia is the lower, the reason probably being that the ammonia has the lower conductivity. It is possible that if correction were made for voltage drop elsewhere in the circuit it would be found that oscillation begins when the decomposition voltage is applied across the solution-mercury surface.

It seemed possible that the rapid oscillation of the drop might be due to an action similar to that in the Wehnelt interruptor. It is found, however, that the same effect is produced if the platinum wire is replaced by a glass tube filled with the same liquid as in the drop (see Fig. 4). The break occurs simply by the drop spreading until it pulls away from the point, and not by any film forming on the platinum. Moreover, the spreading drop is caused to contract by a break anywhere in the circuit.

It would appear that the presence of OH-ions normally tends to prevent spread,

but that when they are driven on to the mercury surface by an electric field, and are able to give up their extra electron, spreading will occur. On reversing the polarity the drop progressively contracts till all the film has disappeared from the mercury. The subsequent deposition of the Na or K-ion on the mercury is accompanied by rapid spreading until the circuit is broken. Thereupon the Na or K on the mercury probably attacks the water forming hydrates which in turn cause the contraction (*see* Section VI).

The explanation, however, is not quite so simple, since this oscillation can be obtained with any solution, unless the conductivity is so high that an arc forms before the necessary voltage is reached. For a drop of conductivity water an E.M.F. of three volts is sufficient to markedly accelerate spreading (mercury positive), or to cause a partial contraction (mercury negative). A great increase in voltage, however, is necessary to make the drop oscillate, 70 volts being necessary for ordinary distilled water, and as much as 400 volts for a drop of conductivity water (in air). Apparently in this case the H-ion produces exactly the same effect as the Na or K-ion above, a much greater voltage being necessary in order to drive sufficient ions on to the mercury. The fact that a field of several thousand volts per centimetre can be applied across a drop of water without producing appreciable electrolysis is in itself interesting evidence of the quality of the water.

Substances that naturally spread rapidly were tested by holding the platinum wire just above the mercury surface (the mercury being negative) and then allowing the drop of solution to run down the wire. Using this device, sodium chloride solution could be prevented from spreading and caused to oscillate. It was even possible to prevent dilute HCl from spreading. With a 0.0002 normal solution of HCl it requires approximately 30 volts to prevent spreading and 250 volts to produce oscillation. For higher concentrations the voltage necessary is so high that an arc forms between point and mercury surface before the value which would prevent spreading is reached.

#### VIII. ADDITIONAL PHENOMENA AND AN IMPROVED MEANS OF OBSERVATION.

(a) *Projection and Photography of Phenomena.*—Photography of thin transparent films on a perfect mercury surface is impossible by ordinary means. The modern "point-o-lite" lamp, however, gives a powerful point source, and if light from such a source is reflected by the mercury surface on to a screen a fairly well defined image of objects on the mercury surface is thrown on the screen. In particular the edges of drops and films show up owing to their curvature interfering with the regular reflection from the mercury surface. This method is of great assistance in observing phenomena, and, further, permits of their exhibition to an audience.

For photography, better definition is secured if the arrangement sketched (*see* Fig. 5) is used. Light from *P* is caused to converge on to the mercury surface *M* and is received on the photo plate after it has converged to a point and is diverging again. Definition is further improved if the lens is left in the camera *C*, and the camera focused as well as possible on to the mercury surface. The foreshortening of the picture in one direction is due to the oblique incidence of the light. This could be reduced by using more nearly normal light in the method, as used by Vincent\* in his photography of ripples on a mercury surface.

\* Phil. Mag., June (1897).

(b) *Ridge Described by Osborne Reynolds*.—A water surface reflects light well enough for the above method of projection to be used, when the phenomena of spreading films show up with a wealth of detail.

As is well known, if a trace of olive oil be dissolved in pure benzol, and the solution added drop by drop to a clean water surface, the first drops flash over the surface and disappear, after showing beautiful film colours. Successive drops spread more and more slowly, down to the stage where sufficient oil has been added to form a monomolecular layer on the surface of the water and drops no longer spread.

Plate No. 10 shows a drop of the solution spreading on a surface of water that has been slightly contaminated. Observation shows that the phenomena are of essentially the same nature with a perfectly clean surface, but then the processes occur too rapidly to be photographed by the method used. The limit of the visible film of benzol is clearly shown in the plate by the Newton's rings. About an inch beyond the visible drop, however, is shown a clearly defined white line, indicating sharp curvature or a ridge on the water surface. This ridge is quite invisible with ordinary methods of illumination, but is easily observed with the arrangement

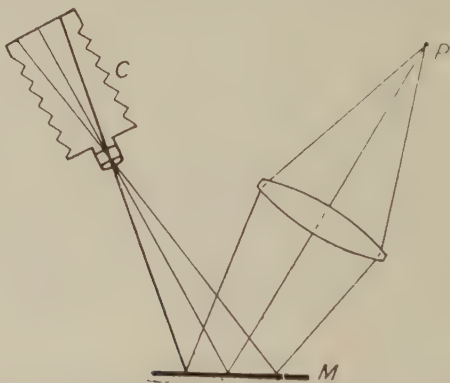


FIG. 5.—ARRANGEMENT FOR PHOTOGRAPHY OF FILMS ON A MERCURY SURFACE.

described. There is little doubt that this is the ridge which Osborne Reynolds observed under certain conditions when grease was spreading on a water surface, and to which Edser\* refers. When a drop of the benzol solution is placed on a clean water surface the ridge travels outward so fast that it is only observed with difficulty. The principle involved in rendering the ridge visible is essentially the same as that employed by Labrouste† in rendering visible the stationary edge of a monomolecular layer of oil on a water surface.

(c) *A Phenomenon shown by a Water Film on a Glass Surface*.—If a perfectly clean glass dish of the kind described above (Section II) be rinsed with water and then held vertically, as it drains a well defined horizontal line, apparently a ridge of water, travels *upward* across the glass. The ridge is thick enough to distort the appearance of objects viewed through the glass, and to focus sunlight shining through the dish into a sharp line of light. If, when the line has travelled half-way

\* B.A.A.S. Fourth Report on Colloid Chemistry, p. 49.

† Ann. de Physique, 14, p. 164.

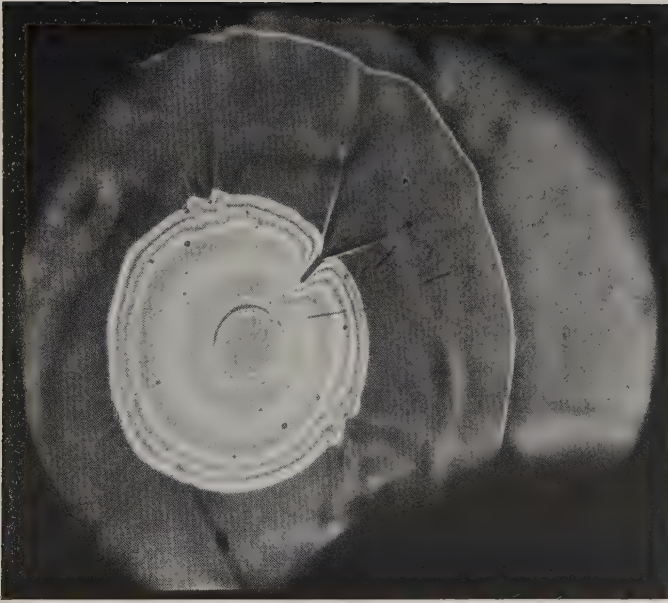


PLATE 10.





across the dish, the latter be rotated through  $90^\circ$  making the line vertical, the lower half of the line swings round into a horizontal position and then continues to travel upward.

The same effect may be seen using a piece of plane glass, though this must be handled by means of a glass rod sealed on to the sheet in order to avoid touching the surface in lifting it from the water. Examined in sodium light, the film of water shows horizontal interference fringes which are crowded together near the ridge, indicating that it is an actual thickening in the water film.

If lycopodium be blown on to the surface after the ridge has commenced to travel across it, it will be seen that there is considerable movement in the surface layer of the film near the ridge. Some particles of the powder may be swept upward an inch or more by the ridge on its passage. Nevertheless, the water goes on draining downward throughout, and if the plate of glass is too large the ridge will fail to reach the top owing to the water film above it becoming too thin.

#### IX. CONCLUSION.

This Paper is mainly a description of phenomena observed in the preliminary work on the subject. The observations confirm the views of certain earlier writers that very minute variations decide the spreading or otherwise of water on mercury, but further show that the number and nature of ions present is an important deciding factor.

Any theory or explanation of the effects observed other than is included in general remarks in the various sections of the Paper would, at this stage, be largely guess work.

In conclusion, the writer wishes to express his thanks to Prof. Kerr Grant for helpful suggestions, encouragement and interest throughout; also to Mr. M. L. Olyphant, B.Sc., for manufacturing the stills used and for assistance both on theoretical and practical points.

#### DISCUSSION.

Mr. EDWIN EDSER read an extract from a communication from Osborne Reynolds to the British Association in 1881, describing the rib or slight elevation formed at the advancing edge of the film formed when an oil spreads over water; Osborne Reynolds concluded from this phenomenon that the forces which produce capillary effects are not confined to attractions between contiguous molecules. Mr. Edser referred to a Paper by Leslie in the *Philosophical Magazine* of 1802, which gives an explanation of the rise of a liquid in a capillary tube; the rise is ascribed to an attraction exerted by the walls of the tube on the neighbouring liquid which results in this liquid being squeezed up the walls, provided that the attraction extends into the liquid to a considerable distance. Reference was next made to a similar explanation of the spreading of oil over water, given by Millikan in a small text-book on physics, entitled "*Mechanics, Molecular Physics and Heat*," published in 1902. The water is assumed to exert an attraction on the oil, extending into the latter to a distance much greater than a molecular diameter, with the result that the oil is squeezed out over the surface until the film of oil attains a thickness of the order of magnitude of the diameter of a molecule of oil, when the spreading virtually ceases. Mr. Edser pointed out that, from the equality of action and reaction, it follows that the oil will exert a squeezing action on the superficial layer of water immediately beneath it, with the result that the advancing edge of the oil will be preceded by a minute ridge of water which has been set in motion. If drops of a solution of permanganate of potash are allowed to sink through the surface of still water, vertical-coloured trails are left behind, and, on touching the surface of the water with a needle moistened with oleic acid, the trails are bent sharply just below the surface and drawn out along the surface; this experiment demonstrates that a thin film of water is set in motion by the advancing film of oil. Some oils, such as hydrocarbons of the type  $C_nH_{2n+2}$  do not spread over water, but form lenticular drops. The shape of the upper surfaces of these drops is instructive. The curvature is uniform except near the edge of a drop, where an abrupt

increase of curvature is observed, giving the appearance, described by Hardy, that the surface is "tucked in" round the edge. The only explanation that can be given of this abrupt increase of curvature is that the water exerts a considerable attraction extending some distance into the oil, with the result that a pressure is produced tending to squeeze the oil out over the water the tendency to spread is, however, successfully withstood by the strongly-curved surface of the oil at the edge of the drop.

Mr. A. V. SLATER: Although Mr. Burdon states in concluding his Paper that any theory would be guesswork at the present stage, his Paper appears to me to afford several further proofs of already fairly well-known theories. At all events it cannot but be helpful to express such phenomena as are relevant in terms of existing theories, if only with the object of stimulating discussion.

1. The "distillation theory" of spreading is still further discountenanced by Mr. Burdon's observations that spreading of water is accelerated by traces of acid and inhibited by traces of alkali, which, of course, would not greatly affect spreading by distillation.

2. According to recent work by Rideal and co-workers (Proc. Roy. Soc.), the spreading of a fatty acid on water is due to a pull across the interface and the fatty acid spreads because it, perforce, has to spread. Now, this tension across the interface is explained by molecular attraction between the COOH groups and the water; in Mr. Burdon's case, the attraction is between a mercury surface and mercury ions in solution. The extent of the area covered during the *rapid* stage, being proportional to the number of molecules of acid present, is in accord with this theory—the attraction across the interface being between mercury atoms in the surface and Hg ions, *plus* their complement of water of hydration, in the solution. Consequently, the film will be more than a molecule thick and should depend on the extent of hydration of the attracted ion. Any water in excess of that required to hydrate the ions will spread slowly at the rate for pure water.

3. The advancing ridge observed on spreading may be due to the frictional resistance offered by the surface.

Mr. A. DE WAELE (communicated): Although unable to be present at this meeting, I have had an opportunity of perusing the advance proofs of this most interesting paper. I invariably feel that great thanks are due to investigators of surface and interface phenomena for their work, owing to the close relation of such problems to cell processes and, perhaps, although the connection may not be so immediately apparent, to molecular dynamics.

A phenomenon which has given me much food for thought, but that has never struck me as of easy demonstration until this evening, is that of the disturbance of the equilibrium thickness of the critical layer by curvature of the phase of higher surface tension. That such critical thickness is modified in the direction of a very substantial increase is evident by the following consideration. Under experimental conditions well known to paint technologists, it is possible to determine the specific absorption of liquid medium necessary to convert a finely-divided solid powder to a paste, the transition from a loose non-wetting powder to a coherent paste possessing incipient adhesion (external wetting power) being quite critical. From the ratio of volumes of solid and liquid phases in the system so obtained, with powders of reasonable uniformity of dispersion and spherical form, considerable divergences are realised from the ratios corresponding to either cubical or hexagonal piling. That the discrepancy should amount to that accounted for by an interfacial layer of liquid one or two molecules thick must certainly be anticipated, but the separating layer actually calculates to a thickness of the order of, very often, one hundred molecules or more. Now, if the right hand term of the Dupré equation referred to by Harkins as the "spreading coefficient" be taken as the reciprocal of the relative thickness of the critical layer for a plane surface, and we take the generally-accepted statement that oleic acid spreads to a monomolecular film on water, we find that this substance marks the lower limit of thickness for liquids which are insoluble in the water phase. Returning to the solid-liquid paste previously referred to, we find that such decidedly polar phases as, let us say, zinc oxide and linseed oil, are in equilibrium at a thickness of oil layer corresponding to about 30 molecules.

There may be several possible explanations accounting for the discrepancy in thickness of the layer surrounding curved surfaces, all of which may be related. In the first place, we have the simple hydrostatic equation connecting free or excess energy with radius of curvature, implying a minimum of free energy at infinite radius of curvature, and considerations of the wedge theory of absorbed molecules may reasonably lead us to expect tension equilibria to differ under the two conditions cited. There would appear to have been published references to the variation of surface tension with mass, but I have been unable to trace them. In any case, it seems somewhat remarkable that this obvious point of interest should hitherto have escaped comment.

# XIX.—ON THE ADVANCE OF PERIHELION OF MERCURY.

By J. T. COMBRIDGE, M.A., M.Sc., Imperial College of Science.

Received November 6, 1925.

(Communicated by PROF. S. CHAPMAN.)

## ABSTRACT.

Attention is called to the infinite possibilities of obtaining the Einstein equation for the orbit of a planet by using Newtonian mechanics with an extended potential function. The merits of the other two "crucial phenomena" as such are discussed from this point of view. It is implied that, observational tests being equally satisfied, Einstein's theory is to be preferred on account of its extensive unity and the spontaneity of its results.

SUPPOSE that in the Einstein theory of general relativity the field is such that the fundamental quadratic form can be written

$$ds^2 = V^2 dt^2 - dl^2, \quad . . . . . (1)$$

where

$$dl^2 = \sum_{i,k} a_{ik} dx_i dx_k \quad (i, k=1, 2, 3) \quad . . . . . (2)$$

is the line-element of three-dimensional space, and  $V$  (a function of the  $x_i$  only, as are also the  $a_{ik}$ ) is the velocity of light at any point of that space. Such a field is said to be static. The equations of motion of a particle moving in such a field are

$$\frac{d^2 x_\mu}{ds^2} + \sum_{\alpha, \beta} \left( \{ \alpha \beta, \mu \} \frac{dx_\alpha}{ds} \frac{dx_\beta}{ds} \right) = 0 \quad (\mu, \alpha, \beta=1, 2, 3, 4).$$

The equation for which  $\mu=4$  reduces to

$$\frac{d}{ds} \left( V^2 \frac{dx_4}{ds} \right) = 0.$$

Putting  $x_4=t$  and integrating, we obtain

$$\frac{dt}{ds} = \frac{a}{V^2},$$

$a$  being a constant of integration. The remaining three equations of motion can then be written

$$\frac{d^2 x_i}{dt^2} = \sum_k a^{ik} \frac{\partial}{\partial x_k} \left( -\frac{1}{2} V^2 \right) + \text{terms involving } \frac{dx_i}{dt} \quad (i, k=1, 2, 3),$$

where the  $a^{ik}$  are the contravariant components associated with the  $a_{ik}$ .

The acceleration at any point, therefore, depends partly on the velocity of the particle itself and partly on a "force function"  $X^i$  defined by

$$X^i = \sum_k a^{ik} X_k; \quad \dot{X}_k = \frac{\partial}{\partial x_k} \left( -\frac{1}{2} V^2 \right) \quad (i, k=1, 2, 3).$$

Thus the initial acceleration of a particle placed initially at rest in the field may



be regarded as due to a field of force derived from a potential function  $-\frac{1}{2}V^2$ . This may be compared with Einstein's result\* that, for weak gravitation and for matter moving with velocities small compared with that of light,  $-\frac{1}{2}V^2$  is (to a first approximation in that case) the Newtonian gravitational potential.

This relatedness between an Einstein quadratic form and a Newtonian potential function is of great use when we wish to examine the distribution of matter giving rise to a certain quadratic form. But the consequence to which it now seems desirable to call attention is the existence of endless possibilities of "explaining" the "crucial phenomena" of Einstein's theory without appeal to that theory.

The well-known quadratic form for the field of the sun is that of Schwarzschild,

$$ds^2 = c^2 \left(1 - \frac{2m}{r}\right) dt^2 - \left(1 - \frac{2m}{r}\right)^{-1} dr^2 - r^2 d\theta^2 - r^2 \sin^2 \theta d\varphi^2 \quad \dots \quad (3)$$

where  $m = \gamma M/c^2$ ,  $M$  being the mass of the sun,  $\gamma$  the constant of gravitation, and  $c$  the velocity of light in the absence of gravitation.

The differential equation giving the orbit of a planet in this field is

$$\frac{d^2 u}{d\varphi^2} + u = \frac{\gamma M}{h^2} + 3 \frac{\gamma M}{c^2} u^2 \quad \dots \quad (1)$$

where  $u = 1/r$ .

Denoting the right-hand side of this equation in the usual way by  $P/(h^2 u^2)$ , where  $P$  is an attracting force per unit mass, it is clear that the rotation of the apse-line can be accounted for under Newtonian mechanics by substituting a new law of force for the usual  $P = \gamma M u^2$ . From such a force  $P$  a corresponding potential  $\Omega$  can be found by integration through the relation

$$P = u^2 \frac{d\Omega}{du} \quad \dots \quad (5)$$

Now (3) is not the only form in which the field of the sun can be expressed. It has been shown explicitly† that the variable  $r$  may be replaced by any function of  $r$ . This is interpreted as equivalent to adopting a different method of measuring  $r$ . Such a substitution in no way affects the amount of rotation of the apse-line of the orbit. To every function  $R$  of  $r$  which may be substituted in (3) corresponds therefore, through (4) and (5), a potential  $\Omega$  which, under Newtonian mechanics and with the appropriate mode of measurement of  $r$ , will yield the required rotation of the apse-line. All these potentials are, however, merely different representations of one and the same field, and it is not this arbitrariness which gives rise to the endless possibilities mentioned above. But in discussing these it is important to obviate the arbitrariness, and to do this we shall adopt a "canonical form" for  $ds^2$ , guided by the researches of Levi-Civita on this point.‡

This geometer has written in (1) and (2)

$$V = c(1 + U), \quad \dots \quad (6)$$

$$a_{ik} = \delta_i^k + e_{ik} \quad (i, k = 1, 2, 3), \quad \dots \quad (7)$$

\* Ann. der Physik, 49, p. 187 (1916).

† Phil. Mag., 45, p. 726 (1923).

‡ Rend. dei Lincei, Ser. 5, 26, ii, p. 307 (1917).

where  $e_i^k$  and  $U$  are small quantities of the first order compared with unity, and  $\delta_i^k$  is equal to unity or zero according as  $i$  is or is not equal to  $k$ . Hence

$$dl^2 = d\sigma^2 + \sum_{i,k} \theta dx_i dx_k,$$

where  $d\sigma^2$  is the line-element of Euclidean space. He then shows that every value of  $U$  satisfying the Einstein gravitational equations for a static field is a solution of

$$\nabla^2 U = 0, \quad . . . . . (8)$$

the Laplacian operator relating to  $d\sigma^2$  and not to  $dl^2$ . Conversely, to every harmonic function  $U$  corresponds a possible Einstein field. Further, by a proper choice of the spatial co-ordinate system, the quadratic form corresponding to any Newtonian potential  $c^2 U$  can, to our order of approximation, be written

$$ds^2 = c^2(1 - 2U)dt^2 - (1 + 2U)d\sigma^2 \quad . . . . . (9)$$

When the co-ordinates are chosen in this way they are referred to by Levi-Civita as canonical. We cannot do better than select our canonical co-ordinate system by the same criterion.

The form to be taken as canonical for the sun's field is, therefore, the "isotropic" form of (3)\*, namely,

$$ds^2 = c^2 \left(1 - \frac{m}{2R}\right)^2 \left(1 + \frac{m}{2R}\right)^{-2} dt^2 - \left(1 + \frac{m}{2R}\right)^4 d\sigma^2 \quad . . . . . (10)$$

which may be obtained from (3) by the transformation

$$r = R \left(1 + \frac{m}{2R}\right)^2 \quad . . . . . (11)$$

The corresponding equation for the orbit becomes

$$\frac{d^2 u}{d\varphi^2} + u = \frac{\gamma M}{h^2} + 6 \frac{\gamma^2 M^2}{c^2 h^2} u \quad . . . . . (12)$$

where now  $u = 1/R$  and powers of  $Mu$  above the second have been neglected. Hence the canonical expression for  $P$  is given by

$$\frac{P}{u^2} = \gamma M + 6 \frac{\gamma^2 M^2}{c^2} u \quad . . . . . (13)$$

and that for  $\Omega$  is, by (5),

$$\Omega = C + \gamma M u + 3 \frac{\gamma^2 M^2}{c^2} u^2 \quad . . . . . (14)$$

$C$  being a constant of integration.

But owing to the weak nature of the sun's field and the consequent approximations which it is permissible to make, any form of  $\Omega$ , which can be expressed in a

\* Hill and Jeffery, *Phil. Mag.*, 41, p. 23 (1921). It is important to notice that (10) agrees with (9) only if we neglect powers of  $mu$  above the first, whereas only powers above the second may be neglected in (12) to obtain the Einstein correction term.

convergent series of ascending powers of  $Mu$  whose second and third terms agree with (11), will yield the desired result for the rotation of the apse-line. Such a potential is given by

$$\Omega = \frac{c^2 p}{6(p+1)} \left( 1 + \frac{6U}{c^2 p} \right)^{p+1} \quad \dots \quad (15)$$

where

$$U = \gamma Mu. \quad \dots \quad (16)$$

This function can be expanded in a series of the kind required provided

$$\left| \frac{6U}{c^2 p} \right| < 1 \quad \dots \quad (17)$$

For  $p=0$  we find

$$\lim_{p \rightarrow 0} \Omega = U$$

so that we revert to the ordinary Newtonian potential. This corresponds with the fact that the quadratic form (9) will not give the Einstein correction term for the motion of the planet; the exact form (10) must be used and approximations made afterwards.

The possibilities thus opened up were forcibly exemplified in a recent interesting Paper by Dr. G. Temple,\* the basis of which was a relation by which mass varied with potential. On that hypothesis the ordinary Newtonian equation

$$\frac{d^2 x_i}{d\tau^2} = \frac{\partial \Omega}{\partial x_i} \quad (i=1, 2, 3) \quad \dots \quad (18)$$

could be used provided a "proper time"  $\tau$  was employed in conjunction with

$$\Omega = \frac{c^2}{4} (1 + kU)^{-2} \quad \dots \quad (19)$$

$k$  is a constant involved in the fundamental relation, and to give the required result for the planet Mercury it must be taken as  $-2/c^2$ .

Now it is not difficult to start with a potential  $\Omega$  given by (15) and to deduce the relation between  $M$  and  $U$  which must exist in order that the equations (18) may be used with the same definition of  $\tau$ . The differential equation in  $M$  and  $U$  proves integrable and the result is

$$\frac{1}{2} K^2 (p+1)(p+2) M^2 U^2 - M_0^2 \{ K U (p+2)(1+KU)^{p+1} - (1+KU)^{p+2} + 1 \} \quad \dots \quad (20)$$

where

$$K = \frac{6}{c^2 p} \quad \dots \quad (21)$$

For  $p=0$ , which, as we have seen, is the Newtonian case, (20) gives  $M=M_0$ . For  $p=-3$  (20) and (21) yield respectively

$$M^2 = M_0^2 (1 + KU)^{-2}; \quad K = -2/c^2;$$

which is the particular case considered by Temple. In a first approximation (20) gives

$$M = M_0 (1 + 2U/c^2)$$

which is independent of  $p$ .

\* Proc. Phys. Soc., Vol. 37, p. 269 (1925). I regret being unable to incorporate Dr. Temple's notation here. His " $U$ " is of the opposite sign to mine.

The description of electromagnetic phenomena on Temple's hypothesis is no argument for his particular "apparent" potential as opposed to any of the other possible ones, since it requires a different value for  $k$  from the one required for gravitation.

For the displacement of lines in the solar spectrum the general relation (20) gives the same result, in a first approximation, for all values of  $p$ , and this result is twice the Einstein shift.

For the deviation of light in passing the sun it is enough to observe that the equation of motion of the light pulse is to be obtained from the exact equation (4) by making  $h$  infinite, the resulting equation being

$$\frac{d^2u}{d\varphi^2} + u = 3mu^2 \quad . . . . . (22)$$

which gives the Einstein deflection of  $4m/\Delta$ , where  $\Delta$  is the perpendicular distance from the centre of the sun to the grazing ray. The light pulse, therefore, behaves like a particle of zero mass, and its deviation is entirely due to the Einstein correction term. Any theory which accounts for the advance of perihelion of Mercury by an emendation of the Newtonian equation of motion will, therefore, account also for the deflection of light in passing the sun, since the same correcting term obtains in each case. Any value of  $p$  in the relation (20) will thus account equally well for the two phenomena.

If it were originally surprising that Einstein should succeed in explaining the outstanding discrepancy in the motion of Mercury, it must have been more surprising since that the discrepancy should be explicable in so many ways. Whitehead's theory of relativity accounted for it, and that in a generous manner, for it contained three laws of gravitation which might be adopted in the absence of an electromagnetic field. The first of these is Einstein's law; the second yields exactly the same equations of motion; the third can be made to do so by appropriate choice of a certain arbitrary function.\* Subsequent theories have aimed rather at accounting for this particular astronomical phenomenon than at building up a consistent theory of space, time and gravitation. But that much was already accomplished under Newtonian mechanics. I am not aware that even the most ardent opponent of Einstein's theory has ever accused him of inventing the theory in order to account for the discrepancy in question. *Ars est celare artem*. If such a charge were true Einstein would deserve even more admiration than has hitherto been accorded to him. The latest theories do not pretend to explain the discrepancy, but yield only a fraction of the usual result, and that in the opposite direction—a consummation devoutly regarded by some, since too close agreement between theory and experience would leave no room for future discovery or for the perturbations due to other planets.

It has not been my purpose to put forward a plausible hypothesis to account either for the single phenomenon under discussion or for the other phenomena which a comprehensive theory is required to explain. Rather have I tried to indicate that the motion of perihelion of Mercury can be accounted for in a very large number

\* Temple, *Phil. Mag.*, 48, p. 277 (1924). This is very different from the arbitrary function occurring in the Schwarzschild solution, for the rate of rotation of the apse-line is the same for *all* values of the latter function; it is not necessary to assign to it a particular expression in order to obtain the correct result.



of ways, of which only a few have so far been advanced, and that consequently its choice in the first place as a "crucial" phenomenon was unfortunate. Seeing how the deviation of light (in passing the sun) is bound up with it, and having regard to the state of our experimental knowledge of the vibration of atoms in a gravitational field,\* it would appear that until an application of Einstein's equations can be found which depends on more than one of the ten coefficients of his fundamental quadratic form there will be little hope of discriminating between his theory and endless others which can be built up by using a single potential or, as Eddington has pleasantly put it, by "tinkering with Newton's equations."

\*ADDENDUM.

Since the above was written it has become known that Einstein's prediction of the spectral shift has been verified in a remarkable manner by observations of the companion of Sirius. It may, therefore, transpire in time that this once disputed and despised phenomenon is the very one of the three advanced as crucial which will be decisive as between various theories. But had the prediction been proved false the fault might have lain not in the relativistic theory but in Einstein's assumption that the period of vibration of the atom is unaffected by a gravitational field. For that reason I am loth to regard the spectral shift as a phenomenon more crucial than the others.

DISCUSSION.

Dr. TEMPLE: A curious difficulty arises in connection with equation (12), which is quoted from the paper by Hill and Jeffery. On making  $h \rightarrow \infty$  in the Schwarzschild equation (4), we obtain the equation to the curvilinear path of a light pulse (22); but on making  $h \rightarrow \infty$  in equation (12), we obtain the equation to a straight line. The solution of this difficulty depends upon an important distinction between the orbital equations obtained from the line-elements due to Schwarzschild and to Hill and Jeffery. The equations of motion derived from both line-elements issue in an equation analogous to Kepler's law of the constancy of areal velocity and in an equation analogous to the Newtonian law of the constancy of the total energy (potential + kinetic). The symbols  $a$  and  $h$  denote constants of integration figuring in these equations and retaining the same numerical value no matter which line-element is made the basis of our argument. In both cases we may deduce from these two equations a third equation which determines the form of the orbit. But, whereas Schwarzschild's line-element leads to an equation involving only the constant  $h$ , the line-element of Hill and Jeffery leads to the equation

$$-\frac{d^2u}{d\varphi^2} + u = \frac{m}{h^2}(2a^2 - c^2) + \frac{m^2u}{2h^2}(15a^2 - 3c^2) \quad \dots \dots \dots (A)$$

which involves both of the constants  $a$  and  $h$ . (N.B.—Powers of  $mu$  higher than the second have been neglected in obtaining equation A.)

In problems of planetary motion we may introduce the approximation—

$$a \doteq c$$

and thus deduce from equation (A) the equation given by Hill and Jeffery and here numbered (12). But in the problem of determining the deviation of rays of light by the sun, not only must we make  $h \rightarrow \infty$ , but also we must let  $a \rightarrow \infty$ , while—

$$\frac{h}{a} \rightarrow \text{a finite constant, } \Delta,$$

subsequently to be identified with the perpendicular from the centre of the sun on to the track of the ray of light. We then obtain from equation (A) the relation—

$$\frac{d^2u}{d\varphi^2} + u = \frac{2m}{\Delta^2} + \frac{15m^2u}{2\Delta^2}$$

which agrees with equation (22) in yielding the result  $4m/\Delta$  for the angular deviation in radians of the light from a distant star.

It is an interesting exercise to deduce equation (A) from the Schwarzschild equation (4) by means of the transformation (11). It may be mentioned that the labour is considerably lightened by identifying not the equations themselves but their first integrals, namely :—

$$\left(\frac{du}{d\varphi}\right)^2 + u^2 = \frac{2m}{h^2}c^2u + 2mu^3 + \frac{a^2 - c^2}{h^2} \text{ (Schwarzschild)}$$

and

$$\left(\frac{du}{d\varphi}\right)^2 + u^2 = \frac{2m}{h^2}(2a^2 - c^2)u + \frac{m^2u^2}{2h^2}(15a^2 - 3c^2) + \frac{a^2 - c^2}{h^2} \text{ (Hill and Jeffery).}$$

AUTHOR'S reply : The difficulty mentioned by Dr. Temple had presented itself to me, but I was satisfied that it was purely analytical. The Schwarzschild solution and the Hill and Jeffery solution are merely different pictures of the same field, and I realised that the invisibility of a certain feature in the second canvas was due not to bad painting but to injudicious hanging. I am grateful to Dr. Temple for so illuminating the scene that the feature in question becomes easily apparent.

The transformation (11) was quoted for transition from (3) to (10).

DEMONSTRATION OF AN INSTRUMENT FOR IMITATING THE EASTWARD  
DEVIATION OF BODIES FALLING FROM A GREAT HEIGHT.

BY G. R. MATHER.

IF a body, initially stationary with respect to the earth, be allowed to drop from a height, it will appear to move eastward as it falls. Newton suggested that this phenomenon might possibly furnish a measure of the earth's rate of rotation, and a photograph of his autograph letter on this subject was shown. The curve showing the trajectory with respect to the earth, as drawn by Newton, was convex to the radius vector drawn to the initial position; and Prof. Rankine, in introducing the demonstration, gave an analysis showing that this drawing is correct. Many astronomical text-books, however, give the curve as a parabola concave to the initial radius vector, and the apparatus is designed to show the true state of the case.

The apparatus comprises a large horizontal rotatable table on which a sheet of paper is mounted. A weight carrying a tracing point is designed to slide easily over the paper and is attached to a thread which passes down through a hole at the centre of the turntable; a second weight is fastened to the other end of the thread, and hangs vertically below the turntable. The table is set in rotation by a gravity motor comprising a weight attached to a string, which is wound round the spindle, and when the motor has gone out of action, so that the speed of rotation is constant, the thread is automatically cut, so that the tracer-weight may be drawn in towards the centre from its initially peripheral position. The curve traced is very similar to that sketched by Newton.

The demonstration acquired a personal interest from the fact that Mr. Mather, who is now 85 years of age, became interested in the subject at the age of 14 through an accident which befell him when playing with a joy-wheel improvised from farm machinery.



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